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The *nf* and *ng* levels of Ar II

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With 3 figures in the text

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I. Introduction

From previous work on the spectrum of singly ionized argon various terms belonging to the p^4ns, np, and nd configurations are known, as well as some 4*f* levels, viz. $(^3P)4f\,^4F$, ^4D, ^2D, two levels ascribed to $(^3P)4f$ but with no designation, and one $(^1D)4f$ level [1]. No *nf* levels with *n* greater than 4 and no *ng* levels are among those previously known.

A new investigation of Ar II has been carried out by the author, including complete and accurate wavelength measurements in the whole 12500–500 Å spectral range with the object of extending the analysis. About 180 new energy levels have now been found and identified, some 120 being based on *nf* and *ng* configurations. These groups of high quantum levels should form an excellent observational basis for a study of the approximate and pronounced pair coupling in the p^4l configuration. The theoretical treatment of the p^4l configuration, which appears not to have been done previously for *l* greater than 2, is presented in this issue of Arkiv för Fysik in

Table 1. K values of the p^4l configuration for pair coupling ($l \geqslant 2$).

Parent level:	$^3P_2$					$^3P_1$			$^3P_0$
K:	$l+2$	$l+1$	l	$l-1$	$l-2$	$l+1$	l	$l-1$	l

Parent level:	$^1D_2$					$^1S_0$
K:	$l+2$	$l+1$	l	$l-1$	$l-2$	l

a paper by N. H. Möller on electronic configurations with one electron outside a shell with two holes in the shell. A comparison between the observed and the theoretical distribution of the levels is included in the present paper.

II. The p^4l configuration

The p^4l configuration, consisting of four equivalent p electrons outside closed shells and an external electron, gives rise to term systems which are based on the $^3P_{2,\,1,\,0}$, $^1D_2$, and $^1S_0$ terms of the p^4 configuration. For low n and l quantum numbers—e.g. 4s, 4p, and 3d in the case of singly ionized argon—LS coupling is valid, giving rise to a quartet and a doublet system based on the ^3P parent term, which is deepest, a doublet system based on $^1D_2$, and one more doublet system based on $^1S_0$. For higher l values the coupling approaches Jl or pair coupling, implying an eletrostatic interaction between the outer electron and the p^4 core which is weak compared to the spin-orbit interaction of the core but strong compared to the spin-orbit interaction of the external electron. The orbital moment of the outer electron $\boldsymbol{l}$ is coupled to the total angular moment of the core, $\boldsymbol{J}_c$, forming the quantized resultant $\boldsymbol{K} = \boldsymbol{J}_c + \boldsymbol{l}$. The coupling between the spin of the outer electron, $\boldsymbol{s}$, and $\boldsymbol{K}$ gives the total angular momentum of the system, $\boldsymbol{J} = \boldsymbol{K} + \boldsymbol{s}$. The two spin orientations correspond to a pair of levels with the same K but with J values differing by unity. Table 1 contains the K values of the p^4l configuration for $l \geqslant 2$. The two J values associated with each K are obtained by adding $\pm\frac{1}{2}$. This gives a total of 30 energy levels for a given nl, if l is greater than 2. To characterize the levels in pair coupling the ($^3P_{2,1,0}$, ^1D, or ^1S) $nl\,[K]_J$ symbols are used.

Electric dipole transitions between Jl coupled terms are governed by the selection rules $\Delta J_c = 0$ and $\Delta K = 0$, or ± 1 in addition to the rules $\Delta l = \pm 1$ and $\Delta J = 0$, or ± 1, which are independent of the coupling. Since the energy matrix is not diagonal in J_c or K, departures from rigorous pair coupling could be accompanied by exceptions from the K and J_c selection rules.

III. Experimental

The argon II spectrum was excited by means of an electrodeless high-frequency discharge using equipment previously described [3, 4, 5]. As appears from the spectrograms reproduced in the papers cited, it is possible to recognize the spectrum lines of singly ionized argon with great certainty by changing the high-frequency pulse power and by observing the corresponding changes of the relative line intensities. This was most advantageous for the following analysis.

The spectrum between 12500 Å and 500 Å was recorded by means of various instruments. The 9900–1900 Å range was covered with a 21-foot, Jarrell-Ash grating spectrograph having a dispersion of about 5 Å/mm in the first order. The second order of the same instrument (dispersion about 2.5 Å/mm) was used for the 4900–2500 Å region. Between 9500 Å and the photographic limit (towards 13000 Å) the first order of another 21-foot grating spectrograph, having a dispersion of about 7.5 Å/mm was used. Second order spectrograms (dispersion about 3.8 Å/mm) were recorded with the same instrument between 5400 and 4700 Å. Previous measurements by the author in the 6000–4200 Å range were made with a large autocollimation glass prism spectrograph [6]. The investigation of the vacuum ultraviolet between 2000 and 500 Å has also been described previously [5].

A description of further experimental details, the characteristics of the spectrographs, the standard lines, the measuring of spectrograms, evaluation of wavelengths, etc. will be given in a forthcoming paper.

The wavelengths on which the present investigation is based are weighted means of measurements on several plates, and their uncertainty is estimated not to exceed 0.02 Å for good lines in the infrared and to be only a few thousandths of an ångström for shorter wavelengths. The corresponding wavenumber uncertainty should be a few hundredths of a cm^{-1} for the main part of the spectrum excluding the vacuum region and the adjacent part of the ultraviolet above 2000 Å. For many lines the accuracy should be better than 0.01 cm^{-1}.

IV. Observed *nf* and *ng* levels and combinations

1. *nf*

The new nf levels were found and identified mainly from combinations with $(^3P)3d$, $(^3P)4d$, and $(^1D)3d$ terms (Fig. 1).

$(^3P)4f$. The $(^3P)3d$–$(^3P)4f$ combinations are all below 2300 Å, partly in the vacuum ultraviolet. Since the coupling of the $(^3P)3d$ configuration is close to LS coupling[1] and $(^3P)4f$ approaches pair coupling, most lines permitted by the selection rules for l and J appear on the spectrograms, there being no further restrictions. Thus, both the quartet and the doublet terms of $(^3P)3d$ combine with $4f$ levels based on all ^3P parent levels ($J_c = 2$, 1, and 0). A good example for this is the $(^3P)3d\,^4P$ and ^2P combinations with $(^3P)4f$, as appears from Table 2.

$(^3P)4d$–$(^3P)4f$ lines were observed in the infrared between 7795 Å and 11068 Å; some predicted combinations, particularly those involving the $(^3P)4d$ doublets, fall beyond the photographic region. The observed $4d$–$4f$ combinations show characteristics which are similar to those of the corresponding $3d$–$4f$ combinations; the intensity relations are also alike.

In Ar II the $(^1D)3d$ doublets are extended over a wide energy range [7] implying the spreading of the $(^1D)3d$–$(^3P)4f$ lines over a large part of the spectrum, viz. between 2385 Å and 9168 Å. More than 50 lines of this kind have been observed, some of them rather strong, e.g. λ 4203, $(^1D)3d\,^2D_{2\frac{1}{2}}$–$(^3P_1)4f[4]_{3\frac{1}{2}}$. Here again the combina-

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[1] The couplings of the $3p^4 4p$ and $3p^4 3d$ configurations will be dealt with in a separate paper.

Table 2. The $(^3P)\,3d$

	$(^3P_2)\ 4f\ [5]_{5\frac{1}{2}}$ 195 123.54	$[5]_{4\frac{1}{2}}$ 195 128.27	$[4]_{4\frac{1}{2}}$ 194 800.18	$[4]_{3\frac{1}{2}}$ 194 822.10	$[3]_{3\frac{1}{2}}$ 194 883.00	$[3]_{2\frac{1}{2}}$ 194 861.27	$[2]_{2\frac{1}{2}}$ 195 031.12	194
$(^3P)\ 3d\ ^4F_{4\frac{1}{2}}$ 142 186.28	6 52 937.2	—	4 52 613.91	1 52 636.2	—			
$^4F_{3\frac{1}{2}}$ 142 717.03		4 52 411.20	2 52 082.90	3 52 105.13	—	—	—	
$^4F_{2\frac{1}{2}}$ 143 107.60				2 51 714.49	1 51 775.35	2 51 753.65	—	
$^4F_{1\frac{1}{2}}$ 143 371.36						—	—	51
$(^3P)\ 3d\ ^4D_{3\frac{1}{2}}$ 132 327.28		—	6 62 472.9	4 62 494.8	1 62 556.3	1 62 534.2	1 62 704.3	
$^4D_{2\frac{1}{2}}$ 132 481.15				5 62 340.9	(m C II 62 400.4)	4 62 380.2	2 62 549.9	62
$^4D_{1\frac{1}{2}}$ 132 630.65						4 62 230.6	(m C II 62 400.4)	62
$^4D_{\frac{1}{2}}$ 132 737.62								62
$(^3P)\ 3d\ ^4P_{2\frac{1}{2}}$ 147 875.87				4 46 946.13	4 47 007.02	3 46 985.55	3 47 155.22	47
$^4P_{1\frac{1}{2}}$ 147 503.03						2 47 358.26	5 47 528.00	47
$^4P_{\frac{1}{2}}$ 147 227.97								47
$(^3P)\ 3d\ ^2F_{3\frac{1}{2}}$ 149 179.17		10 bl Ar II 45 949.36	5 45 621.19	2 45 642.97	6 45 703.63	bl Ar II	1 aff Ar II 45 852.4	
$^2F_{2\frac{1}{2}}$ 150 147.62				2 44 674.43	6 44 735.26	3 aff Ar II 44 713.64	4 44 883.30	1 44
$(^3P)\ 3d\ ^2D_{2\frac{1}{2}}$ 151 087.25				4 43 734.85	7 43 795.74	1 43 774.21	3 aff Ar II 43 944.01	43
$^2D_{1\frac{1}{2}}$ 150 474.90						5 44 386.27	5 44 556.09	2w 44
$(^3P)\ 3d\ ^2P_{1\frac{1}{2}}$ 145 668.81						3 49 192.58	3 49 362.34	49
$^2P_{\frac{1}{2}}$ 144 709.91								50

ations in Ar II (in cm⁻¹).

	$[1]_{\frac{1}{2}}$	$(^3P_1)\ 4f\ [4]_{4\frac{1}{2}}$	$[4]_{3\frac{1}{2}}$	$[3]_{3\frac{1}{2}}$	$[3]_{2\frac{1}{2}}$	$[2]_{2\frac{1}{2}}$	$[2]_{1\frac{1}{2}}$	$(^3P_0)\ 4f\ [3]_{3\frac{1}{2}}$	$[3]_{2\frac{1}{2}}$
.61	195 281.38	196 103.31	196 119.02	196 305.04	196 315.51	196 089.86	196 076.38	196 621.89	196 633.02
		—	—	—				—	
		6 53 386.3	1 53 402.2	1 53 587.9	—	—		—	—
			4 53 011.4	2 53 197.5	1 53 207.9	—	—	3 53 514.3	—
	—				4 52 944.0	—	0.5 52 704.7	—	4 53 261.7
		4 63 776.0	—	1 63 978.1	—	—		—	—
.7			1 63 637.9	1 63 823.9	—	—	—	3 64 140.7	—
.1	1 62 651.1				—	3 63 459.2	—		2 64 002.4
	1 62 544.1						3 63 338.8		
71			1h aff Si II 48 244.08	5 48 429.15	2 48 439.73	4 48 214.05	1 48 200.55	5 48 745.99	2 48 757.16
45	3 47 778.35				2 48 812.59	5 48 586.80	3 48 573.26		2 49 130.05
57	5 48 053.31						3 48 848.45		
		6 46 923.99	—	2 47 125.69	(1 bl Ar II 47 135.86)	—		—	—
3			5 45 971.33	6 46 157.29	—	2 45 942.31	m?	6 46 474.23	2 46 485.27
0			5 45 031.68	m Si I 45 216.54	2 45 228.10	bl Ar II?	2 bl Ar II 44 989.11	5 45 534.60	2 45 545.74
9	—				1w bl Ar II 45 838.97	4 bl Ar II 45 614.69	2 45 601.44		m Ar II 46 157.29
3	—				3 50 646.58	1 50 421.12	1 50 407.52		3 50 964.14
0	—						2 51 366.34		

tions occur between an LS coupled and a nearly pair coupled configuration, and there are apparently no restrictions as regards the parentage of the levels, $3d$ being based on ^1D and $4f$ on $^3P_{2,1,0}$. One single $(^1D)3d$ level, $^2G_{4\frac{1}{2}}$, gives no observed $(^3P)4f$ combination (Table 3).

Some lines of medium intensity in the visible region are $(^3P)4f$ combinations with the $(^1S)3d\,^2D$ term recently identified [7].

A line group of particular interest was found in the ultraviolet, viz. $(^1D)4s\,^2D$–$(^3P)4f$, implying the apparent break-down of the selection rule for l, the orbital momentum of the external electron. A comparison of the characteristics of this group in the 2200–2000 Å range with those of $(^3P)3d\,^2D$–$(^3P)4f$, which falls in an adjacent spectral range, shows that the two line groups are very similar as regards observed combinations and their relative intensities; as a rule the $(^1D)4s$–$(^3P)4f$ lines are somewhat weaker than the $(^3P)3d$ combinations. This comparison of the intensities of the two groups and the relative position of the $(^3P)3d\,^2D$ and $(^1D)4s\,^2D$ terms indicates a strong configuration interaction between the latter two terms. Thus, the term *designated* $(^1D)4s\,^2D$ is characterized by a combination of $(^1D)4s\,^2D$ and $(^3P)3d\,^2D$ eigenfunctions and, consequently, has to a large extent $(^3P)3d\,^2D$ character, inducing the appearance of the lines designated $(^1D)4s\,^2D$–$(^3P)4f$. In fact, the situation is more complicated, since at least all ^2D terms ascribed to $(^3P)3d$, $(^1D)4s$, $(^1D)3d$, and $(^1S)3d$ are characterized by eigenfunctions, which are for each of the terms a combination of definite $(^3P)3d$, $(^1D)4s$, $(^1D)3d$, and $(^1S)3d$ eigenfunctions, which means that each term has more or less taken over the identity of the others.

In addition to the combinations with deeper terms hitherto treated there are also observed $(^3P)4f$ combinations with higher levels. A few weak lines belong to $(^3P)4f$–$(^3P)6d$, among them λ 7802, $(^3P_2)4f[5]_{5\frac{1}{2}}$–$(^3P)6d\,^4F_{4\frac{1}{2}}$. The dominating combinations with higher levels are $(^3P)4f$–$(^3P)ng$, which will be treated in the section headed ng.

$(^3P)5f$. The $(^3P)5f$ combinations show great similarities with those of $(^3P)4f$. Since they are shifted about 10000 cm^{-1} towards shorter wavelengths, all predicted and observed $(^3P)3d$–$(^3P)5f$ lines fall in the vacuum ultraviolet [5]; the $(^3P)4d$–$(^3P)5f$ lines fall in the photographic infrared or at shorter wavelengths, even the combinations involving the $(^3P)4d$ doublets. Several medium intensity combinations with $(^1D)3d$ terms have been observed as well as a few weak $(^1S)3d\,^2D$–$(^3P)5f$ lines, but no combinations with $(^1D)4s\,^2D$ analogous to the above $(^1D)4s\,^2D$–$(^3P)4f$ lines. The nonappearance of $(^1D)4s$–$(^3P)5f$, predicted to fall between 1800 and 1700 Å, should depend not only on smaller line intensities as emitted from the light source but also on the much lower optical speed of the vacuum spectrograph compared to that of the Jarrell-Ash instrument. It is a general observation that the $5f$ combinations are weaker than the analogous $4f$ ones, and that they do not appear when the corresponding $4f$ lines are weak. This is particularly marked when the $4f$ lines fall in a region covered by the Jarrell-Ash spectrograph and the $5f$ lines in a region covered by the slower vacuum spectrograph.

$(^3P)6f$. The $(^3P)6f$ combinations are apparently still weaker and the corresponding multiplets not nearly so complete as those due to $4f$. The $(^3P)3d$, $(^3P)4d$, and $(^1D)3d$ combinations and the effective quantum numbers as extrapolated from $4f$ and $5f$ are nevertheless sufficient to establish and identify the $6f$ levels with one exception, viz. $(^3P_2)6f[1]_{\frac{1}{2}}$. Only two weak combinations appear between the $(^3P)4d$ quartets

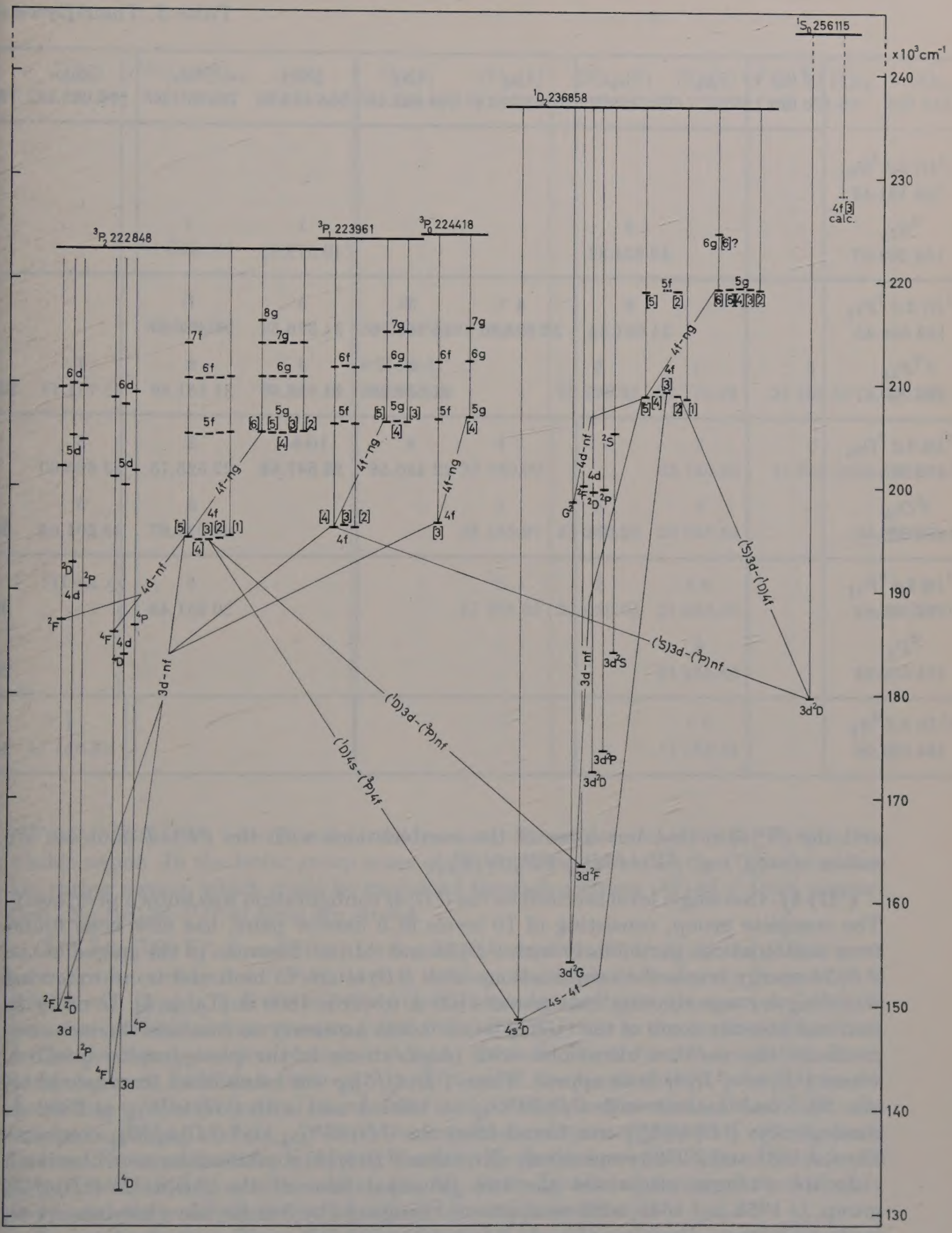

Fig. 1. Partial energy level scheme for Ar II.

Table 3. The (^1D) $3d$ –

	($^3P_2$) $4f$ $[5]_{5\frac{1}{2}}$ 195 123.54	$[5]_{4\frac{1}{2}}$ 195 128.27	$[4]_{4\frac{1}{2}}$ 194 800.18	$[4]_{3\frac{1}{2}}$ 194 822.10	$[3]_{3\frac{1}{2}}$ 194 883.00	$[3]_{2\frac{1}{2}}$ 194 861.27	$[2]_{2\frac{1}{2}}$ 195 031.12	[194
(^1D) $3d$ $^2G_{4\frac{1}{2}}$ 154 181.43								
$^2G_{3\frac{1}{2}}$ 154 203.97		2 40 924.32			1 40 679.03			
(^1D) $3d$ $^2F_{3\frac{1}{2}}$ 163 506.45		8 31 621.84	4 31 293.80	3 31 315.70	5 31 376.58	1 31 354.93		
$^2F_{2\frac{1}{2}}$ 163 299.47				3 31 522.66	6 31 583.56	3 31 561.86	4 31 731.71	31 6
(^1D) $3d$ $^2D_{2\frac{1}{2}}$ 172 335.52				4 22 486.58	10 u 1 22 547.48	2 22 525.75	5 22 695.60	
$^2D_{1\frac{1}{2}}$ 172 829.58						5 22 031.67	5 22 201.54	22
(^1D) $3d$ $^2P_{1\frac{1}{2}}$ 174 409.83						5 20 451.45	m Ar II?	20
$^2P_{\frac{1}{2}}$ 174 820.93								20
(^1D) $3d$ $^2S_{\frac{1}{2}}$ 184 093.06								10

and the (^3P)$6f$ levels, but some of the combinations with the (^3P)$4d$ doublets are rather strong, e.g. (^3P)$4d$ $^2D_{2\frac{1}{2}}$–($^3P_2$)$6f[3]_{3\frac{1}{2}}$.

(^{1}D) 4*f*. One single level ascribed to the (^1D)$4f$ configuration was known previously. The complete group, consisting of 10 levels in 5 narrow pairs, has now been found from combinations particularly with (^1D)$3d$ and (^1D)$4d$. Because of the spread of the (^1D)$3d$ energy levels the combinations with (^1D)$4f$ are to be found in an extended wavelength range running from about 4100 Å towards 1800 Å (Table 4). In order to find and identify some of the (^1D)$4f$ levels it was necessary to combine the measurements in the vacuum ultraviolet with observations in the photographic infrared, where (^1D)$4d$–(^1D)$4f$ lines appear. Thus, (^1D)$4f[5]_{5\frac{1}{2}}$ was established from two lines, viz. the combinations with (^1D)$3d^2G_{4\frac{1}{2}}$ at 1830 Å and with (^1D)$4d^2G_{4\frac{1}{2}}$ at 9802 Å. Analogously, (^1D)$4f[5]_{4\frac{1}{2}}$ was found from the (^1D)$3d^2G_{3\frac{1}{2}}$ and (^1D)$4d^2G_{3\frac{1}{2}}$ combinations, λ 1831 and λ 9793 respectively. No other (^1D)$4f[5]$ combinations were observed.

In the vacuum ultraviolet the two principal lines of the (^1D)$4s$ ^2D–(^1D)$4f[3]$ group, $\lambda\lambda$ 1655 and 1649, with an apparent change of l by 3 units, have been observed, indicating the above-mentioned (^1D)$4s$ ^2D–(^1D)$3d$ ^2D configuration interaction. (^1D)$4f$ also combines with the term systems based on the ^3P and ^1S parents. The nations (cm^{-1}).

$\frac{1}{2}$ 7.61	$[1]_{\frac{1}{2}}$ 195 281.38	$(^3P_1)\,4f\,[4]_{4\frac{1}{2}}$ 196 103.31	$[4]_{3\frac{1}{2}}$ 196 119.02	$[3]_{3\frac{1}{2}}$ 196 305.04	$[3]_{2\frac{1}{2}}$ 196 315.51	$[2]_{2\frac{1}{2}}$ 196 089.86	$[2]_{1\frac{1}{2}}$ 196 076.38	$(^3P_0)\,4f\,[3]_{3\frac{1}{2}}$ 196 621.89	$[3]_{2\frac{1}{2}}$ 196 633.02
		1 41 899.51?							
		6 32 596.86		2 32 798.63	1 32 809.06?				
.22			5 32 819.54	9 bl Ar II 33 005.52		2 32 790.42	1 32 776.89	5 33 322.39	2 33 333.50
			11 23 783.51		4 23 980.00		1 23 740.92	6 24 286.36	2 24 297.51
.04					1 23 485.97	8 23 260.29	2 23 246.84		6 23 803.43
.76					5 21 905.66	2 21 680.04	1 h 21 666.60		5 22 223.19
.71							9 21 255.45		
	1 11 188.31						1 h 11 983.34		

$(^3P)3d$–$(^1D)4f$ lines were found in the vacuum ultraviolet and $(^3P)4d$–$(^1D)4f$ in the visible region. In the latter group some of the combinations with the $(^3P)4d$ doublets are rather strong, which could be explained through a strong $(^3P)4d$–$(^1D)3d$ interaction. No $(^1S)3d$–$(^1D)4f$ lines are strong.

$(^3P)7f$, $(^1D)5f$. In addition to the above complete $(^3P)4f$, $5f$, $6f$ and $(^1D)4f$ term groups, where only one $(^3P)6f$ level is lacking, the analysis has given fragments of $(^3P)7f$, viz. $[5]_{5\frac{1}{2},4\frac{1}{2}}$ and some $(^1D)5f$ levels. Among the latter the narrow $(^1D)5f[5]$ pair was established from the two $(^1D)3d\,^2G$–$(^1D)5f[5]$ lines in the vacuum ultraviolet.

The predicted position of higher $(^1D_2)nf$ terms is above the $^3P_2$ ionization limit, $6f$ by between 1400 and 1800 cm^{-1}, and most of the levels should be auto-ionized. According to the theoretical discussions in the subsequent sections *V* and *VII* only two pairs, $[5]_{5\frac{1}{2},4\frac{1}{2}}$ and $[1]_{1\frac{1}{2},\frac{1}{2}}$, should be uninfluenced by configurations with the same l value. No combinations involving these levels have, however, been observed. All $(^1S)nf$ terms should also be above the $^3P_2$ limit, by several thousand cm^{-1} already at $4f$, and they should be extinguished by auto-ionization.

Energy level values. From the above survey of the nf combinations it follows that the levels can, as a rule, be calculated from spectrum lines in the long wavelength

Table 4. The $(^1D)\,3d - (^1D)\,4f$ combinations (cm^{-1}).

	$(^1D_2)\,4f\,[5]_{5\frac12}$ 208 803.24	$[5]_{4\frac12}$ 208 803.23	$[4]_{4\frac12}$ 209 338.21	$[4]_{3\frac12}$ 209 337.87	$[3]_{3\frac12}$ 209 248.55	$[3]_{2\frac12}$ 209 251.47	$[2]_{2\frac12}$ 208 921.20	$[2]_{1\frac12}$ 208 923.42	$[1]_{1\frac12}$ 208 592.11	$[1]_{\frac12}$ 208 591.77
$(^1D)\,3d\,^2G_{4\frac12}$ 154 181.43	5 54 621.8		1 55 156.9							
$^2G_{3\frac12}$ 154 203.97		5 54 599.3		1 55 133.7						
$(^1D)\,3d\,^2F_{3\frac12}$ 163 506.45			7 45 831.78		4 45 741.95		2 45 414.70			
$^2F_{2\frac12}$ 163 299.47				5 aff Ar II 46 038.25	10 bl Ar II 45 949.36		m?			
$(^1D)\,3d\,^2D_{2\frac12}$ 172 335.52					6 36 912.93	2 36 915.97	6 36 585.61	1 36 587.90	3 36 256.59	
$^2D_{1\frac12}$ 172 829.58						6 36 421.74	1 36 091.60	4 36 093.71	m Ar II ? 35 762	2 bl Ar II 35 762.19
$(^1D)\,3d\,^2P_{1\frac12}$ 174 409.83						1 34 841.69	10 34 511.30	2 34 513.55	10 34 182.21	m Ar II 34 182
$^2P_{\frac12}$ 174 820.93								10 34 102.45	m Ar II 33 770	5 33 770.95
$(^1D)\,3d\,^2S_{\frac12}$ 184 093.06								0 24 830.28	10 w aff Ar II 24 499.01	10 w aff Ar II 24 498.77

Table 5. The *nf* and *ng* energy levels of Ar II ($3p^5\,{}^2P_{1\frac{1}{2}}=0$).

a. nf

Designation	Level	Interval	Designation	Level	Interval
$(^3P_2)\,4f\,[5]_{5\frac{1}{2}}$	195 123.54	4.73	$(^3P_2)\,6f\,[5]_{5\frac{1}{2}}$	210 531.7	3.2
$[5]_{4\frac{1}{2}}$	195 128.27		$[5]_{4\frac{1}{2}}$	210 534.90	
$[4]_{4\frac{1}{2}}$	194 800.18	21.92	$[4]_{4\frac{1}{2}}$	210 438.5	8.6
$[4]_{3\frac{1}{2}}$	194 822.10		$[4]_{3\frac{1}{2}}$	210 447.12	
$[3]_{3\frac{1}{2}}$	194 883.00	− 21.73	$[3]_{3\frac{1}{2}}$	210 477.77	− 13.06
$[3]_{2\frac{1}{2}}$	194 861.27		$[3]_{2\frac{1}{2}}$	210 464.71	
$[2]_{2\frac{1}{2}}$	195 031.12	34.63	$[2]_{2\frac{1}{2}}$	210 527.10	14.12
$[2]_{1\frac{1}{2}}$	194 996.49		$[2]_{1\frac{1}{2}}$	210 512.98	
$[1]_{1\frac{1}{2}}$	195 297.61	16.23	$[1]_{1\frac{1}{2}}$	210 584.88	
$[1]_{\frac{1}{2}}$	195 281.38		$[1]_{\frac{1}{2}}$		
$(^3P_1)\,4f\,[4]_{4\frac{1}{2}}$	196 103.31	15.71	$(^3P_1)\,6f\,[4]_{4\frac{1}{2}}$	211 593.3	13.2
$[4]_{3\frac{1}{2}}$	196 119.02		$[4]_{3\frac{1}{2}}$	211 606.47	
$[3]_{3\frac{1}{2}}$	196 305.04	10.47	$[3]_{3\frac{1}{2}}$	211 663.5?	5.7?
$[3]_{2\frac{1}{2}}$	196 315.51		$[3]_{2\frac{1}{2}}$	211 669.18	
$[2]_{2\frac{1}{2}}$	196 089.86	13.48	$[2]_{2\frac{1}{2}}$	211 586.12	13.85
$[2]_{1\frac{1}{2}}$	196 076.38		$[2]_{1\frac{1}{2}}$	211 572.27	
$(^3P_0)\,4f\,[3]_{3\frac{1}{2}}$	196 621.89	11.13	$(^3P_0)\,6f\,[3]_{3\frac{1}{2}}$	212 071.83	5.15
$[3]_{2\frac{1}{2}}$	196 633.02		$[3]_{2\frac{1}{2}}$	212 076.98	
$(^3P_2)\,5f\,[5]_{5\frac{1}{2}}$	205 100.53	3.79	$(^3P_2)\,7f\,[5]_{5\frac{1}{2}}$	213 807.7	1.7
$[5]_{4\frac{1}{2}}$	205 104.32		$[5]_{4\frac{1}{2}}$	213 809.4	
$[4]_{4\frac{1}{2}}$	204 937.80	13.29	$(^1D_2)\,4f\,[5]_{5\frac{1}{2}}$	208 803.24	0.01
$[4]_{3\frac{1}{2}}$	204 951.09		$[5]_{4\frac{1}{2}}$	208 803.23	
$[3]_{3\frac{1}{2}}$	204 996.09	− 18.50	$[4]_{4\frac{1}{2}}$	209 338.21	0.34
$[3]_{2\frac{1}{2}}$	204 977.59		$[4]_{3\frac{1}{2}}$	209 337.87	
$[2]_{2\frac{1}{2}}$	205 079.07	22.85	$[3]_{3\frac{1}{2}}$	209 248.55	2.92
$[2]_{1\frac{1}{2}}$	205 056.22		$[3]_{2\frac{1}{2}}$	209 251.47	
$[1]_{1\frac{1}{2}}$	205 194.04	13.68	$[2]_{2\frac{1}{2}}$	208 921.20	2.22
$[1]_{\frac{1}{2}}$	205 180.36		$[2]_{1\frac{1}{2}}$	208 923.42	
$(^3P_1)\,5f\,[4]_{4\frac{1}{2}}$	206 132.66	16.28	$[1]_{1\frac{1}{2}}$	208 592.11	0.34
$[4]_{3\frac{1}{2}}$	206 148.94		$[1]_{\frac{1}{2}}$	208 591.77	
$[3]_{3\frac{1}{2}}$	206 245.57	9.66	$(^1D_2)\,5f\,[5]_{5\frac{1}{2},\,4\frac{1}{2}}$	218 940.9	
$[3]_{2\frac{1}{2}}$	206 255.23		$[3]_{3\frac{1}{2}}$	219 164.8?	
$[2]_{2\frac{1}{2}}$	206 120.35	16.90	$[2]_{2\frac{1}{2}}$	219 001.82	1.82
$[2]_{1\frac{1}{2}}$	206 103.45		$[2]_{1\frac{1}{2}}$	219 003.64	
$(^3P_0)\,5f\,[3]_{3\frac{1}{2}}$	206 623.80	7.87			
$[3]_{2\frac{1}{2}}$	206 631.67				

b. ng

Designation	Level	Interval	Designation	Level	Interval
$(^3P_2)\,5g\,[6]_{6\frac{1}{2}}$	205 273.60	− 0.02	$(^3P_2)\,5g\,[4]_{4\frac{1}{2}}$	205 214.71	0.00
$[6]_{5\frac{1}{2}}$	205 273.58		$[4]_{3\frac{1}{2}}$	205 214.71	
$[5]_{5\frac{1}{2}}$	205 211.89	0.13	$[3]_{3\frac{1}{2}}$	205 250.03	0.09
$[5]_{4\frac{1}{2}}$	205 212.02		$[3]_{2\frac{1}{2}}$	205 249.94	

(Table 5, *cont.*)

Designation	Level	Interval	Designation	Level	Interval
$(^3P_2)\,5g\,[2]_{2\frac{1}{2}}$	205 301.00	0.14	$(^3P_2)\,7g\,[5]_{5\frac{1}{2}}$	213 859.24	0.12
$[2]_{1\frac{1}{2}}$	205 300.86		$[5]_{4\frac{1}{2}}$	213 859.36	
$(^3P_1)\,5g\,[5]_{5\frac{1}{2}}$	206 347.82	0.06	$[4]_{4\frac{1}{2}}$	213 860.40	0.11
$[5]_{4\frac{1}{2}}$	206 347.88		$[4]_{3\frac{1}{2}}$	213 860.51	
$[4]_{4\frac{1}{2}}$	206 397.29	0.01	$[3]_{3\frac{1}{2}}$	213 873.57	−0.23
$[4]_{3\frac{1}{2}}$	206 397.30		$[3]_{2\frac{1}{2}}$	213 873.80	
$[3]_{3\frac{1}{2}}$	206 336.99	0.13	$[2]_{2\frac{1}{2}}$	213 891.43	0.21
$[3]_{2\frac{1}{2}}$	206 336.86		$[2]_{1\frac{1}{2}}$	213 891.22	
$(^3P_0)\,5g\,[4]_{4\frac{1}{2}}$	206 819.32	−0.01	$(^3P_1)\,7g\,[5]_{5\frac{1}{2}}$	214 978.85	0.13
$[4]_{3\frac{1}{2}}$	206 819.31		$[5]_{4\frac{1}{2}}$	214 978.98	
$(^3P_2)\,6g\,[6]_{6\frac{1}{2}}$	210 642.60	0.03	$[4]_{4\frac{1}{2}}$	214 997.43	
$[6]_{5\frac{1}{2}}$	210 642.63		$[4]_{3\frac{1}{2}}$	214 996.8?	
$[5]_{5\frac{1}{2}}$	210 607.55	0.14	$[3]_{3\frac{1}{2}}$	214 974.56	
$[5]_{4\frac{1}{2}}$	210 607.69		$[3]_{2\frac{1}{2}}$	214 974.5?	
$[4]_{4\frac{1}{2}}$	210 609.27	0.11	$(^3P_0)\,7g\,[4]_{4\frac{1}{2}}$	215 441.91	−0.21
$[4]_{3\frac{1}{2}}$	210 609.38		$[4]_{3\frac{1}{2}}$	215 441.70	
$[3]_{3\frac{1}{2}}$	210 630.13	0.08	$(^3P_2)\,8g\,[6]_{6\frac{1}{2}}$	215 983.2	−0.1
$[3]_{2\frac{1}{2}}$	210 630.05		$[6]_{5\frac{1}{2}}$	215 983.1	
$[2]_{2\frac{1}{2}}$	210 658.66	0.11	$(^1D_2)\,5g\,[6]_{6\frac{1}{2},\,5\frac{1}{2}}$	219 203.50	
$[2]_{1\frac{1}{2}}$	210 658.55		$[5]_{5\frac{1}{2}}$	219 322.08	0.05
$(^3P_1)\,6g\,[5]_{5\frac{1}{2}}$	211 732.26	0.11	$[5]_{4\frac{1}{2}}$	219 322.03	
$[5]_{4\frac{1}{2}}$	211 732.37		$[4]_{4\frac{1}{2}}$	219 317.47	0.03
$[4]_{4\frac{1}{2}}$	211 761.38	0.01	$[4]_{3\frac{1}{2}}$	219 317.50	
$[4]_{3\frac{1}{2}}$	211 761.39		$[3]_{3\frac{1}{2}}$	219 245.86	
$[3]_{3\frac{1}{2}}$	211 725.69	0.11	$[2]_{2\frac{1}{2}}$	219 152.43	
$[3]_{2\frac{1}{2}}$	211 725.58		Ar III $(^3P_2)$ ***Limit***	***222 848.2***	
$(^3P_0)\,6g\,[4]_{4\frac{1}{2}}$	212 197.89	0.11	$(^3P_1)$ *Limit*	*223 960.3*	
$[4]_{3\frac{1}{2}}$	212 198.00		$(^3P_0)$ *Limit*	*224 418.4*	
$(^3P_2)\,7g\,[6]_{6\frac{1}{2}}$	213 881.02	0.12	$(^1D_2)\,6g\,[6]_{6\frac{1}{2},\,5\frac{1}{2}}$	224 606.35?	
$[6]_{5\frac{1}{2}}$	213 881.14				

ranges; these lines connect the nf levels with $(^3P)4d$, $(^1D)3d$, and $(^1S)3d$ terms, which are accurately known in relation to $(^3P)4p$ and $(^1D)4p$ from the author's unpublished measurements (to appear in Arkiv för Fysik). The $(^3P)4p$ doublets are fixed in relation to the ground term by means of Herzberg's [8] accurate measures for $3p^6\,{}^2S$–$4p\,{}^2S$, ${}^2P$, ${}^2D$ and $3p^5\,{}^2P$–$3p^6\,{}^2S$ in the vacuum ultraviolet. With few exceptions the $(^3P)4f$, $5f$, $6f$ and $(^1D)4f$ levels should be accurate to a few hundredths of a cm^{-1} in relation to the ground term. The accuracy of the intervals between the levels of some nf groups is estimated to be better than 0.01 cm^{-1}. The less accurate levels nearly all belong to $(^3P)6f$. $(^3P_2)6f[5]_{5\frac{1}{2}}$ had to be calculated from a single $(^3P)3d$ combination since the corresponding combination with $(^3P)4d\,{}^4F_{4\frac{1}{2}}$ was not observed with any certainty; a weak line in the visible region was observed, but 1.8 cm^{-1} from the position derived from the $3d$–$6f$ wavenumber. Also $(^3P_2)[4]_{4\frac{1}{2}}$ was calculated from lines in the vacuum range, while $(^3P_2)[4]_{3\frac{1}{2}}$, $(^3P_2)[2]_{1\frac{1}{2}}$, $(^3P_1)[3]_{3\frac{1}{2}}$, and $(^3P_0)[3]_{3\frac{1}{2}}$ were calculated merely from short wavelengths in the ultraviolet above 2000 Å. $(^3P_1)[4]_{4\frac{1}{2}}$ is less accurate because of a blend. In the $(^3P)5f$ configuration $(^3P_2)[4]_{3\frac{1}{2}}$ is less accurate for analogous reasons.

The level values are given in Table 5, from which the pairing of the levels is obvious as is the occurrence of the pairs in distinct groups each based on a separate $3p^4$ parent level, making the assignment of parent levels to the nf levels unambiguous. This is illustrated in Fig. 2, where the $(^3P)4f$, $5f$, and $6f$ levels and the $3p^4\,{}^3P_{2,1,0}$ parent levels are plotted against the energetic center of gravity of each configuration.

2. *ng*

$(^3P)\,ng$. Transitions between hydrogenic $4f$ and $5g$ terms of a singly ionized atom should fall somewhat above 10 000 Å. Since the $4f$ terms of singly ionized argon were found within a distance of some hundred cm^{-1} from the hydrogenic position and the ng levels should be still more hydrogenlike, the $(^3P)4f$–$(^3P)5g$ combinations were looked for in the photographic infrared, where the principal line groups were indeed found in a narrow range between 9586 Å and 9993 Å. Subsequently the analogous $(^3P)4f$–$(^3P)6g$ and $(^3P)4f$–$(^3P)7g$ combinations were identified in the 6315–6508 Å and 5245–5376 Å ranges, respectively. Two weak and hazy (probably from Stark effect) lines, $\lambda\lambda$ 4792 and 4793, gave two $8g$ levels, $(^3P_2)[6]_{6\frac{1}{2}}$ and $[6]_{5\frac{1}{2}}$. No $(^3P)ng$ combinations, except with $(^3P)4f$, were observed.

$(^1D)\,ng$. Several $(^1D)5g$ levels were established from separate lines after the calculation of their approximate positions from the theoretical energy expressions given in Section V.

$(^1S)\,ng$. The predicted position of $(^1S)ng$ is above the $^1D_2$ ionization limit and the levels are certainly auto-ionized.

$4f$–ng. From Tables 6, 7 and 8 it is evident that the combinations between $(^3P)4f$ and $(^3P)ng$ are much more restricted than the $(^3P)3d$–$(^3P)nf$ transitions. For the latter almost no restrictions were noticed except those represented by the l and J selection rules, while, for $4f$–ng, the rules $\Delta J_c = 0$ and $\Delta K = 0, \pm 1$ are valid with few exceptions. Only a few weak lines corresponding to transitions between $4f$ and ng levels based on different $^3P_{2,1,0}$ parent levels have been observed, e.g. $(^3P_2)4f[2]$–$(^3P_1)5g$ $6g[3]$ and $(^3P_1)4f[2]$–$(^3P_2)5g, 6g[3]$.

The violations of the K selection rule are few but striking; they consist of three rather strong lines, $(^3P_2)4f[3]_{3\frac{1}{2}}$–$(^3P_2)ng[5]_{4\frac{1}{2}}$ ($n = 5$, 6, and 7), with the intensities 2, 5 and 3, respectively, and two weaker lines, $(^3P_2)4f[2]_{2\frac{1}{2}}$–$(^3P_2)ng[4]_{3\frac{1}{2}}$ ($n = 5$ and 6), with the intensities 0 and 1, the K change in each case being 2 units. The theoretical background of this breakdown of the K selection rule in spite of the pronounced pair coupling of the ng configuration and the approached pair coupling of $4f$ is treated in Section VI.

Otherwise the intensity relations, as observed qualitatively, are governed by the general rules which predict strong lines when l, K, and J change by unity in the same direction, the stronger the line the higher the J value, at least within each $\Delta K = -1$ group. One exception is $(^3P_2)4f[3]$–$(^3P_2)7g[4]$, but this is a consequence of the interaction between $(^3P_2)4f[3]_{3\frac{1}{2}}$ and $(^3P_2)4f[4]_{3\frac{1}{2}}$, as discussed in Section VI.

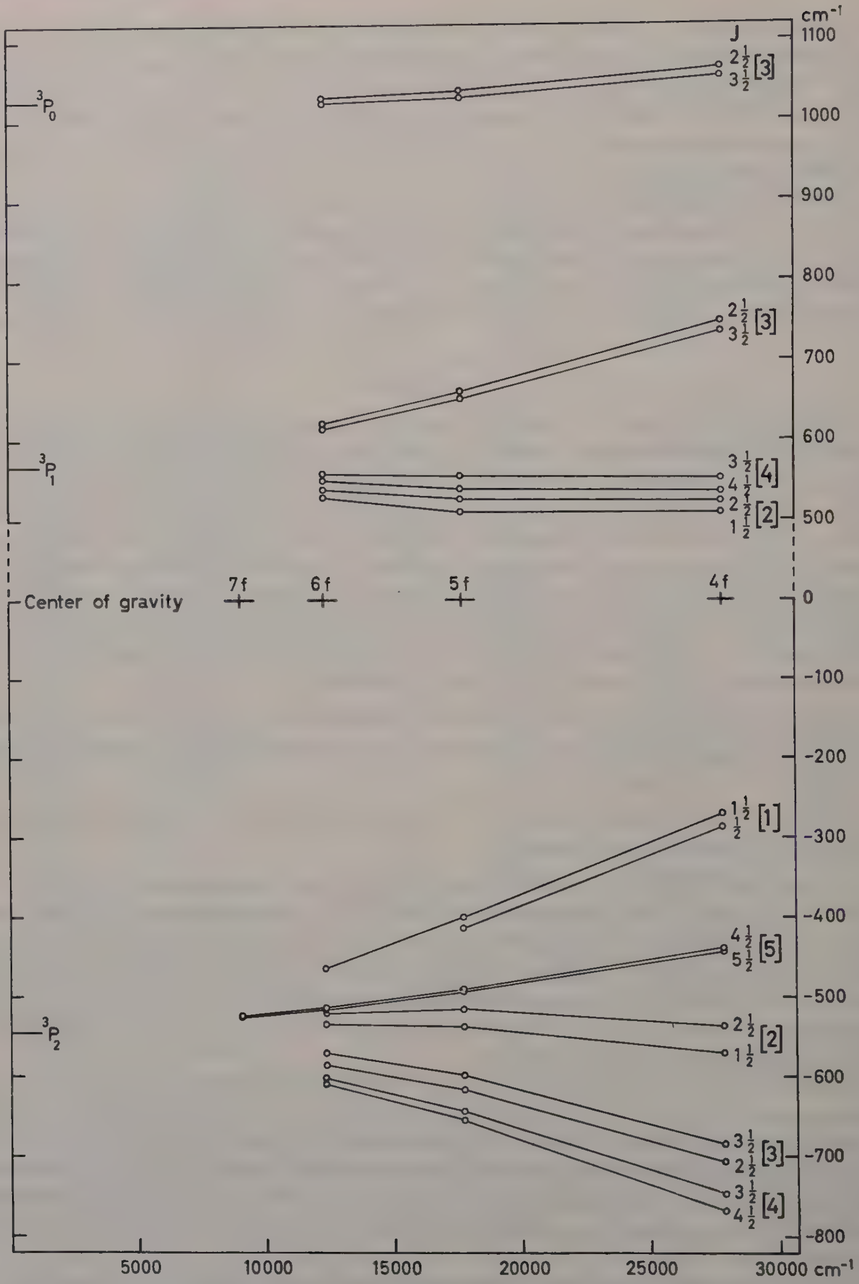

Fig. 2. Centroid diagram of the (^3P)nf series for Ar II.

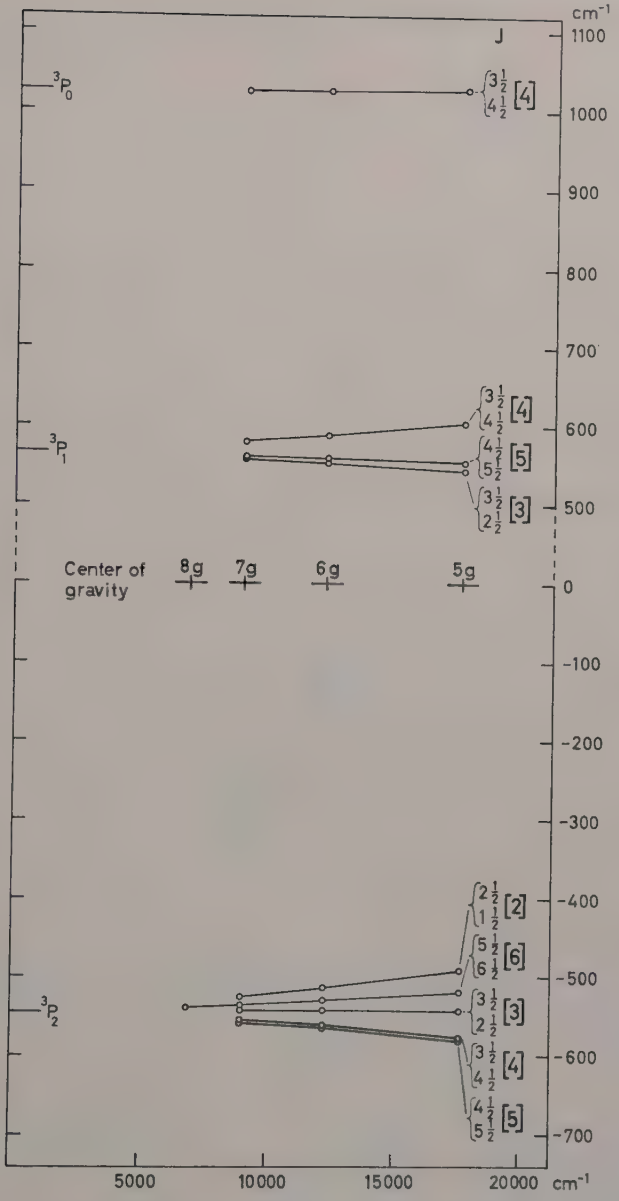

Fig. 3. Centroid diagram for the $(^3P)ng$ series.

Table 6. $(^3P)4f-(^3P)5g$.

	$(^3P_2)\,4f\,[5]_{5\frac{1}{2}}$ 195 123.54	$[5]_{4\frac{1}{2}}$ 195 128.27	$[4]_{4\frac{1}{2}}$ 194 800.18	$[4]_{3\frac{1}{2}}$ 194 822.10	$[3]_{3\frac{1}{2}}$ 194 883.00	$[3]_{2\frac{1}{2}}$ 194 861.27	$[2]_{2\frac{1}{2}}$ 195 031.12	$[2]_{1\frac{1}{2}}$ 194 996.49	$[1]_{1\frac{1}{2}}$ 195 297.61	$[1]_{\frac{1}{2}}$ 195 281.38
$(^3P_2)\,5g\,[6]_{6\frac{1}{2}}$ 205 273.60	10 10 150.06									
$[6]_{5\frac{1}{2}}$ 205 273.58		9 10 145.31								
$[5]_{5\frac{1}{2}}$ 205 211.89	2 10 088.34		7 10 411.71							
$[5]_{4\frac{1}{2}}$ 205 212.02		2 10 083.73		4 10 389.93	*2 10 329.01					
$[4]_{4\frac{1}{2}}$ 205 214.71			2 10 414.54	3 bl Ar II 10 392.62	3 10 331.71					
$[4]_{3\frac{1}{2}}$ 205 214.71				bl Ar II		2 10 353.44	*0 10 183.52?			
$[3]_{3\frac{1}{2}}$ 205 250.03				1 10 427.94	1 10 367.04		3 10 218.91			
$[3]_{2\frac{1}{2}}$ 205 249.94						1 10 388.67		3 10 253.45		
$[2]_{2\frac{1}{2}}$ 205 301.00							1 10 269.87		4 10 003.39	
$[2]_{1\frac{1}{2}}$ 205 300.86						0 10 439.57		1 10 304.37		3 10 019.48

	$(^3P_1)\,4f\,[4]_{4\frac{1}{2}}$ 196 103.31	$[4]_{3\frac{1}{2}}$ 196 119.02	$[3]_{3\frac{1}{2}}$ 196 305.04	$[3]_{2\frac{1}{2}}$ 196 315.51	$[2]_{2\frac{1}{2}}$ 196 089.86	$[2]_{1\frac{1}{2}}$ 196 076.38	$(^3P_0)\,4f\,[3]_{3\frac{1}{2}}$ 196 621.89	$[3]_{2\frac{1}{2}}$ 196 633.02
$(^3P_1)\,5g\,[5]_{5\frac{1}{2}}$ 206 347.82	4 10 244.52							
$[5]_{4\frac{1}{2}}$ 206 347.88		4 10 228.87						
$[4]_{4\frac{1}{2}}$ 206 397.29	1 10 293.95		5 10 092.25					
$[4]_{3\frac{1}{2}}$ 206 397.30		0 10 278.28		4 10 081.80				
$[3]_{3\frac{1}{2}}$ 206 336.99			1 10 031.96		3 10 247.13			
$[3]_{2\frac{1}{2}}$ 206 336.86				1 10 021.38		2 10 260.48		
$(^3P_0)\,5g\,[4]_{4\frac{1}{2}}$ 206 819.32							4 10 197.44	
$[4]_{3\frac{1}{2}}$ 206 819.31				0 10 503.79				3 10 186.29

Table 7. $(^3P)4f-(^3P)6g$.

	$(^3P_2)\,4f\,[5]_{5\frac{1}{2}}$ 195 123.54	$[5]_{4\frac{1}{2}}$ 195 128.27	$[4]_{4\frac{1}{2}}$ 194 800.18	$[4]_{3\frac{1}{2}}$ 194 822.10	$[3]_{3\frac{1}{2}}$ 194 883.00	$[3]_{2\frac{1}{2}}$ 194 861.27	$[2]_{2\frac{1}{2}}$ 195 031.12	$[2]_{1\frac{1}{2}}$ 194 996.49	$[1]_{1\frac{1}{2}}$ 195 297.61	$[1]_{\frac{1}{2}}$ 195 281.38
$(^3P_2)\,6g\,[6]_{6\frac{1}{2}}$ 210 642.60	9 15 519.06									
$[6]_{5\frac{1}{2}}$ 210 642.63		8 15 514.37								
$[5]_{5\frac{1}{2}}$ 210 607.55	3 15 484.02		8 15 807.37							
$[5]_{4\frac{1}{2}}$ 210 607.69		2 15 479.43		5 15 785.59	*5 15 724.69					
$[4]_{4\frac{1}{2}}$ 210 609.27			3 15 809.07	5 15 787.19	6 15 726.28					
$[4]_{3\frac{1}{2}}$ 210 609.38		0 15 481.08		m Ar II		6 15 748.08	*1 15 578.29			
$[3]_{3\frac{1}{2}}$ 210 630.13			1 15 829.93	1 aff Ar II 15 808.00	2 15 747.15		6 15 598.98			
$[3]_{2\frac{1}{2}}$ 210 630.05				1 bl Ar II		3 15 768.77		5 15 633.57		
$[2]_{2\frac{1}{2}}$ 210 658.66					0 15 775.64		2 15 627.56		6 15 361.03	
$[2]_{1\frac{1}{2}}$ 210 658.55						1 15 797.23		2 15 662.05		4 15 377.17

	$({}^3P_1)\,4f\,[4]_{4\frac{1}{2}}$ 196 103.31	$[4]_{3\frac{1}{2}}$ 196 119.02	$[3]_{3\frac{1}{2}}$ 196 305.04	$[3]_{2\frac{1}{2}}$ 196 315.51	$[2]_{2\frac{1}{2}}$ 196 089.86	$[2]_{1\frac{1}{2}}$ 196 076.38	$({}^3P_0)\,4f\,[3]_{3\frac{1}{2}}$ 196 621.89	$[3]_{2\frac{1}{2}}$ 196 633.02
$({}^3P_1)\,6g\,[5]_{5\frac{1}{2}}$ 211 732.26	7 15 628.95							
$[5]_{4\frac{1}{2}}$ 211 732.37		6 15 613.35						
$[4]_{4\frac{1}{2}}$ 211 761.38	m Ar I		7 15 456.34					
$[4]_{3\frac{1}{2}}$ 211 761.39		2 15 642.39		6 15 445.88				m g? 15 128.40?
$[3]_{3\frac{1}{2}}$ 211 725.69			m Ar II		6 15 635.82			
$[3]_{2\frac{1}{2}}$ 211 725.58				1 bl Ar II 15 410.13		5 15 649.20		
$({}^3P_0)\,6g\,[4]_{4\frac{1}{2}}$ 212 197.89							8 15 576.01	
$[4]_{3\frac{1}{2}}$ 212 198.00				1 15 882.49				6 15 564.98

Table 8. $(^3P)\,4f-(^3P)\,7g$.

	$(^3P_2)\,4f\,[5]_{5\frac{1}{2}}$ 195 123.54	$[5]_{4\frac{1}{2}}$ 195 128.27	$[4]_{4\frac{1}{2}}$ 194 800.18	$[4]_{3\frac{1}{2}}$ 194 822.10	$[3]_{3\frac{1}{2}}$ 194 883.00	$[3]_{2\frac{1}{2}}$ 194 861.27	$[2]_{2\frac{1}{2}}$ 195 031.12	$[2]_{1\frac{1}{2}}$ 194 996.49	$[1]_{1\frac{1}{2}}$ 195 297.61	$[1]_{\frac{1}{2}}$ 195 281.38
$(^3P_2)\,7g\,[6]_{6\frac{1}{2}}$ 213 881.02	5 18 757.49									
$[6]_{5\frac{1}{2}}$ 213 881.14		4 18 752.87								
$[5]_{5\frac{1}{2}}$ 213 859.24	1 18 735.71		5 bl Ar II 19 059.06							
$[5]_{4\frac{1}{2}}$ 213 859.36		1 bl Ar II? 18 731.03		3 19 037.24	*3 18 976.37					
$[4]_{4\frac{1}{2}}$ 213 860.40			m Ar II?	3 19 038.30	3 bl Ar II 18 977.41					
$[4]_{3\frac{1}{2}}$ 213 860.51				m Ar II ?		4 18 999.25				
$[3]_{3\frac{1}{2}}$ 213 873.57				1 19 051.50	1 18 990.57		6 bl Ar II 18 842.45			
$[3]_{2\frac{1}{2}}$ 213 873.80						1 19 012.54		3 18 877.31		
$[2]_{2\frac{1}{2}}$ 213 891.43							m Ar II?		3 18 593.82	
$[2]_{1\frac{1}{2}}$ 213 891.22								1 aff Ar II 18 894.80		2 18 609.84

Since the $5g$, $6g$, and $7g$ level values are calculated from lines in the long wavelength range with $4f$ as a base, the accuracy does not differ much from that of the $4f$ levels; the accuracy of the levels in relation to the ground term is estimated to be but a few hundredths of a cm^{-1}, and the intervals between the levels of an ng group should be accurate to about $0.02\ \mathrm{cm}^{-1}$. The pronounced pairing of the levels is obvious from Table 5—the pair splitting is in some cases about $0.2\ \mathrm{cm}^{-1}$ but often much smaller—as well as from the centroid diagram (Fig. 3), which also shows that the assignation of parent levels is unambiguous.

V. Theoretical distribution of p^4f and p^4g levels for pair coupling

1. *Calculation of energy parameters. General aspects*

The derivation of the elements of the energy matrix for p^4l in pair coupling is contained in N. H. Möller's paper on the "Calculation of atomic energy levels for electronic configurations with one electron outside a nearly closed shell and two holes in this shell for LS and pair couplings", published in the present issue of Arkiv för Fysik [2]. The energies of the parent levels $p^4\,{}^1S_0$, ${}^3P_{2,1,0}$, and ${}^1D_2$ are to be found e.g. in the work by Condon and Shortley [9]; for completeness, the coefficients of the Coulomb and exchange integrals and the spin-orbit energy in the diagonal energy expression, $E(\text{parent level}) = \mathfrak{F}^0 + f_2\mathfrak{F}^2 - z\zeta_p$, are given also here (Table 9). The diagonal elements of the p^4l energy matrix have the form $E = E(\text{parent level}) - f_0' F^0 - f_2' F^2 + g_{l-1}' G^{l-1} + g_{l+1}' G^{l+1}$, where the Coulomb and exchange integrals, F^0, F^2, G^{l-1}, and G^{l+1} are defined in the work cited [10]. The coefficient f_0' equals 2, and for the remaining coefficients, f_2', g_{l-1}', and g_{l+1}', general expressions are given in Table II in Möller's paper [2].

Since the energy matrix is diagonal in J, the non-diagonal elements occur between levels with equal J values. Non-diagonal f_2' exist between levels with equal K values, based on different parent levels, viz. ${}^1S$–${}^1D$, ${}^3P_0$–${}^3P_2$, and ${}^3P_1$–${}^3P_2$. Non-diagonal g_{l-1}' and g_{l+1}' occur between levels with K values which are equal or differing by ± 1, based on the same or on different parents. No non-diagonal f_0' exist. The appearance of appreciable non-diagonal $g_{l\pm 1}'$ between levels with different values of K means that K is not a very good quantum number, i.e. that the pair coupling is not very pronounced.

In the electron systems considered, the radial parts of the electronic wave functions are not known with sufficient accuracy to permit the explicit calculation of the energy integrals, F^0, F^2, G^{l-1}, and G^{l+1}. But since the energy integrals are common to a whole configuration, a convenient method to compare the theoretical energy expressions with the observed energies is to use the energy integral symbols as parameters, which are determined from the observations and, then, to compare the observed levels with those calculated from the parameters. The method implies that the number of energy expressions is larger than the number of parameters. For each p^4f or p^4g configuration there are theoretically 30 energy levels as compared with 6 parameters, viz. $\mathfrak{F}^0$–$2F^0$, $\mathfrak{F}^2$, ζ_p, F^2, G^{l-1}, and G^{l+1}. If the comparison is restricted to levels based on ${}^3P_{2,1,0}$ there are 18 levels and 5 parameters, since all levels have a common f_2 which is $-\frac{3}{5}$. In that case the parameters are $\mathfrak{F}^0 - \frac{3}{5}\mathfrak{F}^2 - 2F^0$, ζ_p, F^2, G^{l-1}, and G^{l+1}.

Provided the parameters are known, the energy levels can be computed in two

Table 9. Diagonal f_2 and z coefficients for the p^4 configuration.

Level	J	f_2	z
^1S	0	0	0
^3P	0	$-\frac{3}{5}$	-1
	1		$-\frac{1}{2}$
	2		$\frac{1}{2}$
^1D	2	$-\frac{9}{25}$	0

steps. First, the energies corresponding to the diagonal expressions only are computed, and then the final energies are obtained by introducing the non-diagonal elements into secular equations with the "diagonal" energies as starting values. A reverse procedure in order to compute the parameters is not possible, since the observed energies cannot be divided into a "diagonal" and a "non-diagonal" part. The diagonality of the energy matrix with respect to J implies, however, that the energy sum of all levels within a configuration, which have the same J, is independent of non-diagonal elements. Consequently, the calculation of the parameters can be based on sums of diagonal energy expressions. If a given level is not connected to any other level through a non-diagonal element, the diagonal energy expression for that single level may be used in the parameter calculations.

The representation of the energy level distribution in parameter form is restricted to separate configurations, while possible non-diagonal elements between different configurations, especially between analogous configurations with different n values, must be accounted for by other means. This can, in principle, be done theoretically with the aid of a sufficiently accurate treatment of the corresponding Schrödinger equation, or phenomenologically, from interaction parameters as derived from the observations. The occurrence of such interactions is further discussed in Section VII. The important problem of eliminating the influence of non-diagonal matrix elements in calculating the energy parameters has one more aspect. Since the magnitude of the influence is determined not only by the magnitude of the matrix elements but also by the distance between interacting levels, the calculations should, as far as possible, be based on level groups, which have a large distance from interacting levels. Therefore, in the present investigation of $3p^4nf$ and $3p^4ng$ the parameter calculations were based on the level groups based on the $^3P_{2,1,0}$ parents alone even in those cases where it would be possible to include the levels based on ^1D, since the latter are often near other $3p^4nl$ groups, with the same l but with a different n, based on ^3P. $(^1D)4f$, for example, is near $(^3P)5f$ and $(^3P)6f$. In the energy sum expressions for (^3P) levels, only those non-diagonal elements are eliminated which are associated with levels based on $^3P_{2,1,0}$. The influence of non-diagonal elements between $(^3P)nl$ and $(^1D)nl$ is, however, negligible, as realized from a subsequent calculation based on the G^{l-1} and G^{l+1} parameters; F^2 has theoretically no influence, since there are no non-diagonal f_2 between levels based on ^3P and ^1D. This is also true for levels based on ^3P and ^1S.

The spin-orbit interaction of the *external* electron is estimated to be small as compared to the electrostatic interaction and is not included in the calculations.

In the presentation of the calculations for the $3p^4nf$ ($n = 4, 5$) and $3p^4ng$ ($n = 5, 6, 7$) configurations we shall start with ng, which shows the most pronounced pair coupling.

2. *ng levels computed from diagonal and non-diagonal matrix elements. Comparison with observations.*

The explicit diagonal energy expressions for ng are:

$$
\begin{aligned}
({}^3P_2)\,ng\,[6]_{6\frac{1}{2}} &= A - \tfrac{1}{2}\zeta_p + \tfrac{4}{55}F^2 \\
[6]_{5\frac{1}{2}} &= \quad + \tfrac{4}{55}F^2 \qquad\qquad + \tfrac{39}{121}G^5 \\
[5]_{5\frac{1}{2}} &= \quad - \tfrac{1}{11}F^2 \qquad\qquad + \tfrac{6}{121}G^5 \\
[5]_{4\frac{1}{2}} &= \quad - \tfrac{1}{11}F^2 + \tfrac{11}{35}G^3 + \tfrac{28}{121}G^5 \\
[4]_{4\frac{1}{2}} &= \quad - \tfrac{13}{154}F^2 + \tfrac{11}{90}G^3 + \tfrac{98}{1089}G^5 \\
[4]_{3\frac{1}{2}} &= \quad - \tfrac{13}{154}F^2 + \tfrac{1045}{3528}G^3 + \tfrac{7}{72}G^5 \\
[3]_{3\frac{1}{2}} &= \quad + \tfrac{1}{70}F^2 + \tfrac{95}{392}G^3 + \tfrac{7}{88}G^5 \\
[3]_{2\frac{1}{2}} &= \quad + \tfrac{1}{70}F^2 + \tfrac{15}{98}G^3 \\
[2]_{2\frac{1}{2}} &= \quad + \tfrac{1}{7}F^2 + \tfrac{15}{49}G^3 \\
[2]_{1\frac{1}{2}} &= \quad + \tfrac{1}{7}F^2
\end{aligned}
$$

$$
\begin{aligned}
({}^3\mathrm{P}_1)\,ng\,[5]_{5\frac{1}{2}} &= A + \tfrac{1}{2}\zeta_p - \tfrac{2}{55}F^2 \qquad\qquad + \tfrac{9}{121}G^5 \\
[5]_{4\frac{1}{2}} &= \quad - \tfrac{2}{55}F^2 + \tfrac{22}{105}G^3 + \tfrac{388}{1815}G^5 \\
[4]_{4\frac{1}{2}} &= \quad + \tfrac{1}{10}F^2 + \tfrac{1}{210}G^3 + \tfrac{2}{15}G^5 \\
[4]_{3\frac{1}{2}} &= \quad + \tfrac{1}{10}F^2 + \tfrac{5}{24}G^3 + \tfrac{1}{264}G^5 \\
[3]_{3\frac{1}{2}} &= \quad - \tfrac{1}{14}F^2 + \tfrac{367}{1176}G^3 + \tfrac{35}{264}G^5 \\
[3]_{2\frac{1}{2}} &= \quad - \tfrac{1}{14}F^2 + \tfrac{9}{98}G^3
\end{aligned}
$$

$$
\begin{aligned}
({}^3P_0)\,ng\,[4]_{4\frac{1}{2}} &= A + \zeta_p \qquad + \tfrac{4}{63}G^3 + \tfrac{14}{99}G^5 \\
[4]_{3\frac{1}{2}} &= \qquad\qquad + \tfrac{13}{63}G^3 + \tfrac{5}{99}G^5
\end{aligned}
$$

$$
\begin{aligned}
({}^1D_2)\,ng\,[6]_{6\frac{1}{2},\,5\frac{1}{2}} &= A + \tfrac{6}{25}\mathfrak{J}^2 - \tfrac{8}{55}F^2 \qquad\qquad + \tfrac{30}{121}G^5 \\
[5]_{5\frac{1}{2},\,4\frac{1}{2}} &= \quad + \tfrac{2}{11}F^2 \qquad\qquad + \tfrac{12}{121}G^5 \\
[4]_{4\frac{1}{2},\,3\frac{1}{2}} &= \quad + \tfrac{13}{77}F^2 + \tfrac{55}{441}G^3 + \tfrac{28}{1089}G^5 \\
[3]_{3\frac{1}{2},\,2\frac{1}{2}} &= \quad - \tfrac{1}{35}F^2 + \tfrac{15}{49}G^3 \\
[2]_{2\frac{1}{2},\,1\frac{1}{2}} &= \quad - \tfrac{2}{7}F^2 + \tfrac{24}{49}G^3
\end{aligned}
$$

$$
({}^1S_0)\,ng\,[4]_{4\frac{1}{2},\,3\frac{1}{2}} = A + \tfrac{3}{5}\mathfrak{J}^2 \qquad + \tfrac{8}{63}G^3 + \tfrac{10}{99}G^5
$$

The pair coupling symbols represent the energy values, and A is substituted for $\mathfrak{J}^0 - \frac{3}{5}\mathfrak{J}^2 - 2F^0$.

By taking only the above diagonal expressions into account the following pair splittings are obtained:

$$
\begin{aligned}
({}^3P_2)\,ng\,[6]_{5\frac{1}{2}}-[6]_{6\frac{1}{2}} &= \qquad\qquad +\tfrac{39}{121}\,G^5\\
[5]_{4\frac{1}{2}}-[5]_{5\frac{1}{2}} &= \tfrac{11}{35}\,G^3+\tfrac{2}{11}\,G^5\\
[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}} &= \tfrac{341}{1960}\,G^3+\tfrac{7}{968}\,G^5\\
[3]_{3\frac{1}{2}}-[3]_{2\frac{1}{2}} &= \tfrac{5}{56}\,G^3+\tfrac{7}{88}\,G^5\\
[2]_{2\frac{1}{2}}-[2]_{1\frac{1}{2}} &= \tfrac{15}{49}\,G^3
\end{aligned}
$$

$$
\begin{aligned}
({}^3P_1)\,ng\,[5]_{4\frac{1}{2}}-[5]_{5\frac{1}{2}} &= \tfrac{22}{105}\,G^3+\tfrac{23}{165}\,G^5\\
[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}} &= \tfrac{57}{280}\,G^3-\tfrac{57}{440}\,G^5\\
[3]_{3\frac{1}{2}}-[3]_{2\frac{1}{2}} &= \tfrac{37}{168}\,G^3+\tfrac{35}{264}\,G^5
\end{aligned}
$$

$$({}^3P_0)\,ng\,[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}} = \tfrac{1}{7}\,G^3-\tfrac{1}{11}\,G^5$$

For pairs based on ${}^1D$ and ${}^1S$ the splittings are theoretically zero, disregarding the influence of non-diagonal elements and the influence of the spin-orbit interaction of the external electron. The splitting expressions for the $({}^3P)ng$ pairs depend only on the G^{l-1} and G^{l+1} integrals. If the latter approach zero, the splittings and also the contribution of non-diagonal G^{l-1} and G^{l+1} elements to the total energy become very small.

The following sums of diagonal expressions, extended over levels based on ${}^3P_{2,\,1,\,0}$ with equal n and J values, should, according to theory, be independent of non-diagonal f_2', g_{l-1}' and g_{l+1}' between the levels included:

$$
\begin{aligned}
[6]_{6\frac{1}{2}} &= A-\tfrac{1}{2}\zeta_p+\tfrac{4}{55}F^2\\
\sum_{K=5}^{6}[K]_{5\frac{1}{2}} &= 3A-\tfrac{1}{2}\zeta_p-\tfrac{3}{55}F^2+\tfrac{54}{121}G^5\\
\sum_{K=4}^{5}[K]_{4\frac{1}{2}} &= 5A+\zeta_p-\tfrac{43}{385}F^2+\tfrac{5}{7}G^3+\tfrac{98}{121}G^5\\
\sum_{K=3}^{4}[K]_{3\frac{1}{2}} &= 5A+\zeta_p-\tfrac{16}{385}F^2+\tfrac{62}{49}G^3+\tfrac{4}{11}G^5\\
\sum_{K=2}^{3}[K]_{2\frac{1}{2}} &= 3A-\tfrac{1}{2}\zeta_p+\tfrac{3}{35}F^2+\tfrac{27}{49}G^3\\
[2]_{1\frac{1}{2}} &= A-\tfrac{1}{2}\zeta_p+\tfrac{1}{7}F^2
\end{aligned}
$$

The A, ζ_p, F^2, G^3, and G^5 parameters might be calculated by least squares from the last six equations, but G^3 and G^5 are several orders of magnitude smaller than F^2 and, therefore, it was preferred to compute them separately by least squares from the pair-splitting equations. This appeared to be permissible for $5g$ and $6g$ since a subsequent calculation showed that the influence of non-diagonal elements on the splittings did not exceed 0.01 cm^{-1}. Some observed $7g$ splittings are uncertain and therefore G^3 and G^5 were calculated from $[2]_{2\frac{1}{2}}-[2]_{1\frac{1}{2}}$ and $[6]_{5\frac{1}{2}}-[6]_{6\frac{1}{2}}$, respectively, which are theoretically not affected by any non-diagonal f_2'; for $7g$ the G^3 and G^5 values are uncertain.

The theoretical interval ratio of the $p^4\,{}^3P$ term is $({}^3P_2-{}^3P_1)/({}^3P_1-{}^3P_0)=2$, considering only diagonal energy matrix elements, while that observed for Ar III is 1112.1/458.1 = 2.43. Because of this discrepancy, which partly depends on the influence of

Table 10. Selected non-diagonal energy matrix elements for the $({}^3P)ng$ configuration.

	f_2'	g_3'	g_5'
$({}^3P_2)\ [5]_{5\frac{1}{2}}$–$({}^3P_1)\ [5]_{5\frac{1}{2}}$	$+\frac{3\sqrt{6}}{55}$		$+\frac{3\sqrt{6}}{121}$
$[5]_{4\frac{1}{2}}$– $[5]_{4\frac{1}{2}}$	$+\frac{3\sqrt{6}}{55}$	$-\frac{11\sqrt{6}}{105}$	$-\frac{32\sqrt{6}}{1815}$
$[4]_{4\frac{1}{2}}$– $[4]_{4\frac{1}{2}}$	$-\frac{3\sqrt{231}}{770}$	$+\frac{\sqrt{231}}{630}$	$+\frac{26\sqrt{231}}{5445}$
$[4]_{3\frac{1}{2}}$– $[4]_{3\frac{1}{2}}$	$-\frac{3\sqrt{231}}{770}$	$-\frac{25\sqrt{231}}{3528}$	$+\frac{\sqrt{231}}{792}$
$[3]_{3\frac{1}{2}}$– $[3]_{3\frac{1}{2}}$	$-\frac{3\sqrt{15}}{70}$	$+\frac{41\sqrt{15}}{1176}$	$+\frac{7\sqrt{15}}{264}$
$[3]_{2\frac{1}{2}}$– $[3]_{2\frac{1}{2}}$	$-\frac{3\sqrt{15}}{70}$	$-\frac{3\sqrt{15}}{98}$	
$({}^3P_2)\ [4]_{4\frac{1}{2}}$–$({}^3P_0)\ [4]_{4\frac{1}{2}}$	$+\frac{2\sqrt{770}}{385}$	$-\frac{\sqrt{770}}{315}$	$+\frac{2\sqrt{770}}{5445}$
$[4]_{3\frac{1}{2}}$– $[4]_{3\frac{1}{2}}$	$+\frac{2\sqrt{770}}{385}$	$-\frac{\sqrt{770}}{882}$	$-\frac{\sqrt{770}}{396}$

	g_3'	g_5'
$({}^3P_2)\ [6]_{5\frac{1}{2}}$–$({}^3P_2)\ [5]_{5\frac{1}{2}}$		$+\frac{3\sqrt{26}}{121}$
$[5]_{4\frac{1}{2}}$– $[4]_{4\frac{1}{2}}$	$+\frac{11\sqrt{14}}{210}$	$+\frac{14\sqrt{14}}{363}$
$[4]_{3\frac{1}{2}}$– $[3]_{3\frac{1}{2}}$	$+\frac{95\sqrt{11}}{1176}$	$+\frac{7\sqrt{11}}{264}$
$[3]_{2\frac{1}{2}}$– $[2]_{2\frac{1}{2}}$	$+\frac{15\sqrt{2}}{98}$	
$({}^3P_1)\ [5]_{4\frac{1}{2}}$–$({}^3P_1)\ [4]_{4\frac{1}{2}}$	$-\frac{\sqrt{11}}{105}$	$+\frac{56\sqrt{11}}{1815}$
$[4]_{3\frac{1}{2}}$– $[3]_{3\frac{1}{2}}$	$+\frac{87\sqrt{35}}{3528}$	$+\frac{\sqrt{35}}{264}$

non-diagonal $z\zeta_p$ elements between the ${}^3P$ and the ${}^1D$ and ${}^1S$ levels of the $3p^4$ configuration [9], it was considered suitable to use the observed Ar III splittings (${}^3P_2 = 0$, ${}^3P_1 = 1112.10$, ${}^3P_0 = 1570.20$) instead of ζ_p in the calculations. Therefore, the first two terms in the general energy expressions were replaced in the following way: $A - \frac{1}{2}\zeta_p = B$ (for levels based on ${}^3P_2$), $A + \frac{1}{2}\zeta_p = B + 1112.10$ (for ${}^3P_1$ levels), $A + \zeta_p = B + 1570.20$ (for ${}^3P_0$ levels) and, analogously, $A + \frac{6}{25}\mathfrak{F}^2 = B + 14010.0$ (for levels based on ${}^1D_2$), $A + \frac{3}{5}\mathfrak{F}^2 = B + 33265.7$ (for ${}^1S$ levels).

Finally the G^3 and G^5 parameter values were inserted in the energy sum expressions, and F^2 and B computed by least squares.

It is convenient in the numerical calculations to use integral coefficients, as obtained by the substitutions: $F^2 = 770\,F_2$, $G^3 = 17\,640\,G_3$, and $G^5 = 43\,560\,G_5$.

Non-diagonal elements. Several non-diagonal g_3' and g_5' have a negligible influence on the energies. This is always true of elements between levels based on different parent levels, provided that the levels are not also connected by a non-diagonal f_2'. Such $g_{l\pm1}'$ elements are not included in Table 10 containing selected non-diagonal f_2' and $g_{l\pm1}'$ for $({}^3P)ng$. The energies calculated from the diagonal expressions, using the parameter values found, were introduced as starting values into the secular equations, which are of the third degree for $J = 5\frac{1}{2}$ and $2\frac{1}{2}$ and of the fifth degree for $J = 4\frac{1}{2}$ and $3\frac{1}{2}$. The non-diagonal matrix elements of the energy matrix of $({}^3P)ng$ are, however, so small in comparison to the diagonal energy difference between the levels, $\nu_i^0 - \nu_k^0$, that they may be calculated from the secular equations in their simplified form, $\Delta\nu = \Sigma(H_{ik}^2/(\nu_i^0 - \nu_k^0))$, where H_{ik} represents the non-diagonal matrix elements and ν_i^0, ν_k^0 the diagonal energy matrix elements between the perturbed levels.

***Results for* (^3P) 5g, 6g, 7g.** The F^2, G^3, G^5 and B parameters for $5g$, $6g$ and $7g$ are collected in Table 11, and the energies computed from them in Table 12, containing the energies from the diagonal expressions only in one column, and those considering the non-diagonal elements in the next, the difference thus representing the non-

Table 11. The F^2, G^3, G^5, and B parameters for (^3P) $5g$, $6g$ and $7g$ as calculated from the diagonal matrix elements.

	F^2	G^3	G^5	B
$5g$	371.3	0.3_5	0.1_0	205 247.47
$6g$	215.5	0.4_0	0.1_7	210 627.53
$7g$	136.4	0.6_9*	0.3_4*	213 871.57

* less certain

Table 12. Comparison between observed and calculated (^3P) $5g$, $6g$ and $7g$ levels.

	$5g$			$6g$			$7g$		
	ν (calc)*	ν (calc)	ν (obs)	ν (calc)*	ν (calc)	ν (obs)	ν (calc)*	ν (calc)	ν (obs)
$(^3P_2)$ $[6]_{6\frac{1}{2}}$	205 274.47	274.47	273.60	210 643.20	643.20	642.60	213 881.49	881.49	881.02
$[6]_{5\frac{1}{2}}$	274.50	274.50	273.58	643.26	643.26	642.63	881.60	881.60	881.14
$[5]_{5\frac{1}{2}}$	213.72	211.55	211.89	607.95	607.21	607.55	859.19	858.89	859.24
$[5]_{4\frac{1}{2}}$	213.85	211.69	212.02	608.10	607.36	607.69	859.47	859.13	859.36
$[4]_{4\frac{1}{2}}$	216.18	213.98	214.71	609.41	608.67	609.27	860.17	859.92	860.40
$[4]_{3\frac{1}{2}}$	216.24	214.04	214.71	609.48	608.73	609.38	860.29	859.99	860.51
$[3]_{3\frac{1}{2}}$	252.87	249.36	250.03	630.72	629.55	630.13	873.72	873.26	873.57
$[3]_{2\frac{1}{2}}$	252.82	249.30	249.94	630.67	629.50	630.05	873.63	873.16	873.80
$[2]_{2\frac{1}{2}}$	300.62	300.62	301.00	658.43	658.43	658.66	891.26	891.26	891.43
$[2]_{1\frac{1}{2}}$	300.51	300.51	300.86	658.31	658.31	658.55	891.05	891.05	891.22
$(^3P_1)$ $[5]_{5\frac{1}{2}}$	206 346.08	348.25	347.82	211 731.80	732.54	732.26	214 978.74	979.04	978.85
$[5]_{4\frac{1}{2}}$	346.16	348.32	347.88	731.91	732.64	732.37	978.92	979.21	978.98
$[4]_{4\frac{1}{2}}$	396.71	397.12	397.29	761.20	761.34	761.38	997.36	997.42	997.43
$[4]_{3\frac{1}{2}}$	396.77	397.18	397.30	761.26	761.40	761.39	997.45	997.51	996.8?
$[3]_{3\frac{1}{2}}$	333.17	336.68	336.99	724.38	725.55	725.69	974.19	974.65	974.56
$[3]_{2\frac{1}{2}}$	333.08	336.60	336.86	724.28	725.45	725.58	973.99	974.46	974.5?
$(^3P_0)$ $[4]_{4\frac{1}{2}}$	206 817.70	819.49	819.32	212 197.78	198.39	197.89	215 441.86	442.10	441.91
$[4]_{3\frac{1}{2}}$	817.74	819.53	819.31	197.82	198.43	198.00	441.93	442.17	441.70

* Calculated from diagonal elements only.

Table 13. Comparison between observed and calculated pair splittings for (^3P) $5g$, $6g$, and $7g$.

	$5g$			$6g$			$7g$		
	$\Delta\nu$ (calc)*	$\Delta\nu$ (calc)	$\Delta\nu$ (obs)	$\Delta\nu$ (calc)*	$\Delta\nu$ (calc)	$\Delta\nu$ (obs)	$\Delta\nu$ (calc)*	$\Delta\nu$ (calc)	$\Delta\nu$ (obs)
$(^3P_2)$ $[6]_{5\frac{1}{2}}-[6]_{6\frac{1}{2}}$	0.03	0.03	−0.02	0.06	0.06	0.03	0.11	0.11	0.12
$[5]_{4\frac{1}{2}}-[5]_{5\frac{1}{2}}$	0.13	0.14	0.13	0.15	0.15	0.14	0.28	0.24	0.12
$[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}}$	0.06	0.06	0.00	0.07	0.06	0.11	0.12	0.07	0.11
$[3]_{3\frac{1}{2}}-[3]_{2\frac{1}{2}}$	0.05	0.06	0.09	0.05	0.05	0.08	0.09	0.10	−0.23
$[2]_{2\frac{1}{2}}-[2]_{1\frac{1}{2}}$	0.11	0.11	0.14	0.12	0.12	0.11	0.21	0.21	0.21
$(^3P_1)$ $[5]_{4\frac{1}{2}}-[5]_{5\frac{1}{2}}$	0.08	0.07	0.06	0.11	0.10	0.11	0.18	0.17	0.13
$[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}}$	0.06	0.06	0.01	0.06	0.06	0.01	0.09	0.09	[1]
$[3]_{3\frac{1}{2}}-[3]_{2\frac{1}{2}}$	0.09	0.08	0.13	0.10	0.10	0.11	0.20	0.19	[1]
$(^3P_0)$ $[4]_{3\frac{1}{2}}-[4]_{4\frac{1}{2}}$	0.04	0.04	−0.01	0.04	0.04	0.11	0.07	0.07	−0.21

* Calculated from diagonal expressions only.

[1] One level uncertain.

diagonal influence. The observed levels are also included, and it is seen that the agreement between observed and calculated values is good, the difference amounting to between 0.0 and 0.9 cm^{-1}. It is striking that these discrepancies are quite systematic; the calculated $(^3P_2)[6]$ and $(^3P_1)[5]$ pairs, for example, are regularly higher than those observed, while the contrary holds for $(^3P_2)[5]$ and $(^3P_2)[4]$. It is obvious that the consideration of non-diagonal elements makes the agreement much better for some levels, e.g. $(^3P_1)[3]$ $(n=5,\ 6)$ and $(^3P_0)5g[4]$, but somewhat poorer for others. The small G^3 and G^5 parameters imply small corresponding changes of the energies even when the interacting levels are close to each other. Thus non-diagonal g_3' and g_5' between $(^3P_2)6g[5]_{4\frac{1}{2}}$ and $(^3P_2)6g[4]_{4\frac{1}{2}}$, which are only about 1.5 cm^{-1} apart, correspond to an energy change which is only 0.01 cm^{-1}. For $5g$ and $6g$ no energy changes associated with non-diagonal g_3' and g_5' are larger than this. The $(^3P_2)7g[5]_{4\frac{1}{2}}-[4]_{4\frac{1}{2}}$ interaction as calculated from G^3 and G^5 is 0.05 cm^{-1}, but this result is less accurate.

Small G^3 and G^5 integrals imply small pair splittings as appears from Table 13, containing observed and calculated splittings. The non-diagonal elements cause but small changes in the splittings calculated from the diagonal expressions; for $5g$ and $6g$ the change is at most 0.01 cm^{-1}. The agreement between observed and calculated pair splittings is satisfactory for $5g$ and $6g$ but for $7g$ there are discrepancies which partly should be ascribed to uncertainties of the observed splittings because of blended lines.

The deep $(^3P)5g$ terms are far away from other ng levels, the distance to $(^1D)5g$ being more than 12000 cm^{-1}. Since, according to theory, there is no non-diagonal f_2' between the (^3P) and (^1D) level systems, and since the G^3 and G^5 integrals are small, the calculated $(^3P)5g-(^1D)5g$ interaction is completely negligible, i.e. smaller than 0.01 cm^{-1}. As regards the analogous $(^3P)6g$, $7g-(^1D)5g$ interactions the angular factors of the matrix elements are the same as in the $n=n'$ case but the F^2, G^3, and G^5

Table 14. Observed $(^1D)\,4f-(^1D)\,5g$ combinations.

	$(^1D)\ 4f\ [5]_{5\frac{1}{2}}$ 208 803.24	$[5]_{4\frac{1}{2}}$ 208 803.23	$[4]_{4\frac{1}{2}}$ 209 338.21	$[4]_{3\frac{1}{2}}$ 209 337.87
$(^1D)\ 5g$				
$[6]_{6\frac{1}{2},\,5\frac{1}{2}}$ 219 203.50	(2) 10.400.26			
$[5]_{5\frac{1}{2}}$ 219 322.08	(1) 10 518.82		(1) 9 983.87	
$[5]_{4\frac{1}{2}}$ 219 322.03				(1) 9 984.16
	$[3]_{3\frac{1}{2}}$ 209 248.55	$[3]_{2\frac{1}{2}}$ 209 251.47	$[2]_{2\frac{1}{2}}$ 208 921.20	$[1]_{1\frac{1}{2}}$ 208 592.11
$(^1D)\ 5g$				
$[4]_{4\frac{1}{2}}$ 219 317.47	(1) 10 068.92			
$[4]_{3\frac{1}{2}}$ 219 317.50		(1) 10 066.03		
$[3]_{3\frac{1}{2}}$ 219 245.86			(0) 10 324.66	
$[2]_{2\frac{1}{2}}$ 219 152.43				(0) 10 560.32

integrals are different. These parameters were not determined in the actual case, and therefore it was not possible to compute the magnitude of the interaction energies. But since there are no non-diagonal f_2' involved, and since the G^3 and G^5 integrals are estimated to be small, and, furthermore, the distance between the $(^3P)6g$, $7g$ and $(^1D)5g$ levels is several thousand cm^{-1}, the corresponding interaction energies should be very small.

$(^1D)\,ng$. The $(^1D)5g$ levels were found in the following way. Their positions were computed from the diagonal energy expressions of $(^1D)\,ng$ using the F^2, G^3, G^5, and B parameters calculated from the $(^3P)5g$ observations as given in Table 11. Their combinations with $(^1D)4f$ were looked for and, in fact, found close to their predicted positions. Thus, for $(^1D)5g[6]$ the calculated value is 219203.49 and that obtained from the $(^1D)4f[5]$ combination, λ 9612.508 (int. 2), 219203.50. The observed combinations are given in Table 14, and the comparison between observed and calculated level values in Table 15. The values of the F^2 and $A+\frac{6}{25}\mathfrak{J}^2$ parameters as calculated by least squares from the observed $(^1D)5g[6]$, [5], and [4] terms are 362.4 and 219256.20, respectively. The energies computed from them and from G^3 and G^5 (Table 11) are also given in Table 15. The good agreement between these values and those observed is a strong support for the correctness of the identifications.[1]

An analogous investigation of the $(^1D)6g$ levels shows that they are situated above the ^3P ionization limits. The question then arises whether they are affected by autoionization or not. A study of the non-diagonal energy matrix elements shows that there are no such elements between $(^1D)\,ng[6]_{6\frac{1}{2},\,5\frac{1}{2}}$ or $[2]_{2\frac{1}{2},\,1\frac{1}{2}}$ and any other $n'g$ level. It is noteworthy that there are no interactions between $(^1D)\,ng[6]_{6\frac{1}{2},\,5\frac{1}{2}}$ and $(^3P)\,ng[6]_{6\frac{1}{2},\,5\frac{1}{2}}$

---

[1] Since for the $^1D_2$ parent the spin $S=0$ and, consequently, $J=L$, the f_2', g_{l-1}', and g_{l+1}' coefficients of $(^1D)\,nl$ for pair coupling are the same as for LS coupling; since, further, the G^3 and G^5 integrals are small for $l=4$, the distribution of $(^1D_2)\,ng$ levels is accurately described solely by means of the F^2 parameter and the f_2' coefficients for LS or pair coupling.

Table 15. Observed and calculated $(^1D)\ 5g$ levels.

	ν (calc)[1]	ν (calc)[2]	ν (obs)
$(^1D)\ 5g\ [6]$	219 203.49	203.51	203.50
$[5]_{5\frac{1}{2}}$	219 324.98	322.10	322.08
$[5]_{4\frac{1}{2}}$			322.03
$[4]_{4\frac{1}{2}}$	219 320.19	317.42	317.47
$[4]_{3\frac{1}{2}}$			317.50
$[3]_{3\frac{1}{2}}$	219 246.97	245.96	245.86
$[2]_{2\frac{1}{2}}$	219.151.56	152.83	152.43

[1] Computed from the parameters of Tab. 11.

[2] Computed from the parameters obtained from the $(^1D)\ 5g\ [6]$, [5], [4] observations: $F^2 = 362.4$, $A + \frac{6}{25}\mathfrak{J}^2 = 219\,256.20$.

or between $(^1D)ng[2]_{2\frac{1}{2},1\frac{1}{2}}$ and $(^3P)ng[2]_{2\frac{1}{2},1\frac{1}{2}}$, in spite of the fact that the levels have equal J_c, l, K, and J values. The $(^1D)ng[6]_{6\frac{1}{2},5\frac{1}{2}}$ and $[2]_{2\frac{1}{2},1\frac{1}{2}}$ series should therefore exist above the ^3P limits unaffected by the $(^3P)ng$ continuum. The levels were computed for $n = 6$ and $n = 7$ from the parameters obtained from the $(^3P)6g$ and $7g$ observations (Table 11). The result for $(^1D)6g[6]$ is 224 606.23; the line λ 6326.117, which is somewhat weaker than $(^1D)4f[5]$–$(^1D)5g[6]$, was identified as the analogous $6g$ combination giving for $(^1D)6g[6]$ 224 606.35. The existence of the corresponding $7g$ level could not be settled experimentally, since a strong identified line is close to the predicted wavelength of $(^1D)4f[5]$–$(^1D)7g[6]$. No $6g[2]_{2\frac{1}{2},1\frac{1}{2}}$ combination was observed; nor was it expected as the analogous $5g$ combination is already very weak.

3. *Calculation of nf levels. Comparison with observations*

The explicit diagonal energy expressions for the p^4f configuration are:

$$
\begin{aligned}
(^3P_2)\,nf\,[5]_{5\frac{1}{2}} &= A - \tfrac{1}{2}\zeta_p + \tfrac{1}{15}F^2 \\
[5]_{4\frac{1}{2}} &= + \tfrac{1}{15}F^2 + \tfrac{11}{27}G^4 \\
[4]_{4\frac{1}{2}} &= - \tfrac{1}{10}F^2 + \tfrac{1}{18}G^4 \\
[4]_{3\frac{1}{2}} &= - \tfrac{1}{10}F^2 + \tfrac{27}{56}G^2 + \tfrac{145}{504}G^4 \\
[3]_{3\frac{1}{2}} &= - \tfrac{11}{150}F^2 + \tfrac{9}{56}G^2 + \tfrac{145}{1512}G^4 \\
[3]_{2\frac{1}{2}} &= - \tfrac{11}{150}F^2 + \tfrac{78}{175}G^2 + \tfrac{5}{42}G^4 \\
[2]_{2\frac{1}{2}} &= + \tfrac{1}{25}F^2 + \tfrac{52}{175}G^2 + \tfrac{5}{63}G^4 \\
[2]_{1\frac{1}{2}} &= + \tfrac{1}{25}F^2 + \tfrac{6}{25}G^2 \\
[1]_{1\frac{1}{2}} &= + \tfrac{4}{25}F^2 + \tfrac{9}{25}G^2 \\
[1]_{\frac{1}{2}} &= + \tfrac{4}{25}F^2
\end{aligned}
$$

$$\begin{aligned}
({}^3P_1)\,nf\,[4]_{4\frac{1}{2}} &= A + \tfrac{1}{2}\zeta_p - \tfrac{1}{30}F^2 + \tfrac{5}{54}G^4 \\
[4]_{3\frac{1}{2}} &= -\tfrac{1}{30}F^2 + \tfrac{81}{280}G^2 + \tfrac{401}{1512}G^4 \\
[3]_{3\frac{1}{2}} &= +\tfrac{1}{10}F^2 + \tfrac{3}{280}G^2 + \tfrac{9}{56}G^4 \\
[3]_{2\frac{1}{2}} &= +\tfrac{1}{10}F^2 + \tfrac{2}{7}G^2 + \tfrac{1}{126}G^4 \\
[2]_{2\frac{1}{2}} &= -\tfrac{2}{25}F^2 + \tfrac{76}{175}G^2 + \tfrac{10}{63}G^4 \\
[2]_{1\frac{1}{2}} &= -\tfrac{2}{25}F^2 + \tfrac{3}{25}G^2
\end{aligned}$$

$$\begin{aligned}
({}^3P_0)\,nf\,[3]_{3\frac{1}{2}} &= A + \zeta_p + \tfrac{3}{35}G^2 + \tfrac{11}{63}G^4 \\
[3]_{2\frac{1}{2}} &= + \tfrac{2}{7}G^2 + \tfrac{4}{63}G^4
\end{aligned}$$

$$\begin{aligned}
({}^1D_2)\,nf\,[5]_{5\frac{1}{2},4\frac{1}{2}} &= A + \tfrac{6}{25}\mathfrak{F}^2 - \tfrac{2}{15}F^2 + \tfrac{8}{27}G^4 \\
[4]_{4\frac{1}{2},3\frac{1}{2}} &= +\tfrac{1}{5}F^2 + \tfrac{1}{9}G^4 \\
[3]_{3\frac{1}{2},2\frac{1}{2}} &= +\tfrac{11}{75}F^2 + \tfrac{36}{175}G^2 + \tfrac{5}{189}G^4 \\
[2]_{2\frac{1}{2},1\frac{1}{2}} &= -\tfrac{2}{25}F^2 + \tfrac{12}{25}G^2 \\
[1]_{1\frac{1}{2},\frac{1}{2}} &= -\tfrac{8}{25}F^2 + \tfrac{18}{25}G^2
\end{aligned}$$

$$({}^1S_0)\,nf\,[3]_{3\frac{1}{2},2\frac{1}{2}} = A + \tfrac{3}{5}\mathfrak{F}^2 + \tfrac{6}{35}G^2 + \tfrac{8}{63}G^4.$$

Here $A = \mathfrak{F}^0 - \frac{3}{5}\mathfrak{F}^2 - 2F^0$. For reasons analogous to those stated for ng the following substitutions were made: $({}^3P_2){:}\,A - \frac{1}{2}\zeta_p = B$; $({}^3P_1){:}\,A + \frac{1}{2}\zeta_p = B + 1112.10$; $({}^3P_0){:}\,A + \zeta_p = B + 1570.20$; $({}^1D_2){:}\,A + \frac{6}{25}\mathfrak{F}^2 = B + 14\,010.0$; $({}^1S_0){:}\,A + \frac{3}{5}\mathfrak{F}^2 = B + 33\,265.7$, where 0, 1112.10, 1570.20, 14010.0, and 33265.7 are the observed $3p^4\,{}^3P_{2,1,0}$, ${}^1D_2$, and ${}^1S_0$ levels, respectively, of Ar III. Integral f_2', g_2', and g_4' coefficients were introduced by substituting: $F^2 = 150\,F_2$, $G^2 = 1400\,G_2$, and $G^4 = 1512\,G_4$.

The F^2, G^{l-1}, and G^{l+1} integrals of the nf configurations are much larger than those of ng for equivalent n values and, therefore, the effect of non-diagonal elements is, in most cases, too large to permit a numerical calculation of the G^{l-1} and G^{l+1} parameters from pair interval expressions as given by the diagonal energy formulas. There are two pairs, however, where the influence is small, viz. $({}^3P_2)[5]_{4\frac{1}{2}}$–$[5]_{5\frac{1}{2}}$ and $({}^3P_2)[1]_{1\frac{1}{2}}$–$[1]_{\frac{1}{2}}$. There are no non-diagonal elements between $({}^3P_2)[5]_{5\frac{1}{2}}$ or $({}^3P_2)[1]_{\frac{1}{2}}$ and any other nf level, and no f_2' between $({}^3P_2)[5]_{4\frac{1}{2}}$ or $({}^3P_2)[1]_{1\frac{1}{2}}$ and other nf levels; the influence of non-diagonal $g_{l\pm1}'$ on $({}^3P_2)[5]_{4\frac{1}{2}}$ is unimportant and on $({}^3P_2)[1]_{1\frac{1}{2}}$ less than 1 cm^{-1}. The calculation of the B, F^2, G^2, and G^4 parameters was therefore made on the basis of these two pair-splitting expressions and the diagonal sum expressions for the levels based on ${}^3P_{2,1,0}$.

$$\begin{aligned}
({}^3P_2)\,[5]_{4\frac{1}{2}} - [5]_{5\frac{1}{2}} &= \tfrac{11}{27}G^4 \\
({}^3P_2)\,[1]_{1\frac{1}{2}} - [1]_{\frac{1}{2}} &= \tfrac{9}{25}G^2
\end{aligned}$$

$$\begin{aligned}
[5]_{5\frac{1}{2}} &= A - \tfrac{1}{2}\zeta_p + \tfrac{1}{15}F^2 \\
\sum_{K=4}^{5}[K]_{4\frac{1}{2}} &= 3\,A - \tfrac{1}{2}\zeta_p - \tfrac{1}{15}F^2 + \tfrac{5}{9}G^4
\end{aligned}$$

Table 16. Important non-diagonal matrix elements for $(^3P)\,nf$.

	f_2'	g_2'	g_4'
$(^3P_2)\,[4]_{4\frac{1}{2}}-(^3P_1)\,[4]_{4\frac{1}{2}}$	$+\frac{\sqrt{15}}{30}$		$+\frac{\sqrt{15}}{54}$
$[4]_{3\frac{1}{2}}-\quad[4]_{3\frac{1}{2}}$	$+\frac{\sqrt{15}}{30}$	$-\frac{27\sqrt{15}}{280}$	$-\frac{17\sqrt{15}}{1512}$
$[3]_{3\frac{1}{2}}-\quad[3]_{3\frac{1}{2}}$	$-\frac{\sqrt{15}}{50}$	$+\frac{3\sqrt{15}}{280}$	$+\frac{11\sqrt{15}}{504}$
$[3]_{2\frac{1}{2}}-\quad[3]_{2\frac{1}{2}}$	$-\frac{\sqrt{15}}{50}$	$-\frac{6\sqrt{15}}{175}$	$+\frac{\sqrt{15}}{126}$
$[2]_{2\frac{1}{2}}-\quad[2]_{2\frac{1}{2}}$	$-\frac{3\sqrt{2}}{25}$	$+\frac{24\sqrt{2}}{175}$	$+\frac{5\sqrt{2}}{63}$
$[2]_{1\frac{1}{2}}-\quad[2]_{1\frac{1}{2}}$	$-\frac{3\sqrt{2}}{25}$	$-\frac{3\sqrt{2}}{25}$	
$(^3P_2)\,[3]_{3\frac{1}{2}}-(^3P_0)\,[3]_{3\frac{1}{2}}$	$+\frac{2\sqrt{30}}{75}$	$-\frac{3\sqrt{30}}{140}$	$+\frac{\sqrt{30}}{378}$
$[3]_{2\frac{1}{2}}-\quad[3]_{2\frac{1}{2}}$	$+\frac{2\sqrt{30}}{75}$	$-\frac{2\sqrt{30}}{175}$	$-\frac{\sqrt{30}}{63}$

	g_2'	g_4'
$(^3P_2)\,[5]_{4\frac{1}{2}}-(^3P_2)\,[4]_{4\frac{1}{2}}$		$+\frac{\sqrt{66}}{54}$
$(^3P_2)\,[4]_{3\frac{1}{2}}-(^3P_2)\,[3]_{3\frac{1}{2}}$	$+\frac{9\sqrt{3}}{56}$	$+\frac{145\sqrt{3}}{1512}$
$(^3P_2)\,[3]_{2\frac{1}{2}}-(^3P_2)\,[2]_{2\frac{1}{2}}$	$+\frac{26\sqrt{6}}{175}$	$+\frac{5\sqrt{6}}{126}$
$(^3P_2)\,[2]_{1\frac{1}{2}}-(^3P_2)\,[1]_{1\frac{1}{2}}$	$+\frac{3\sqrt{6}}{25}$	
$(^3P_1)\,[4]_{3\frac{1}{2}}-(^3P_1)\,[3]_{3\frac{1}{2}}$	$-\frac{9\sqrt{3}}{280}$	$+\frac{37\sqrt{3}}{504}$
$(^3P_1)\,[3]_{2\frac{1}{2}}-(^3P_1)\,[2]_{2\frac{1}{2}}$	$+\frac{16\sqrt{5}}{175}$	$+\frac{\sqrt{5}}{63}$

$$\sum_{K=3}^{4}[K]_{3\frac{1}{2}}=5A+\zeta_p-\tfrac{8}{75}F^2+\tfrac{36}{35}G^2+\tfrac{62}{63}G^4$$

$$\sum_{K=2}^{3}[K]_{2\frac{1}{2}}=5A+\zeta_p-\tfrac{1}{75}F^2+\tfrac{306}{175}G^2+\tfrac{3}{7}G^4$$

$$\sum_{K=1}^{2}[K]_{1\frac{1}{2}}=3A-\tfrac{1}{2}\zeta_p+\tfrac{8}{25}F^2+\tfrac{18}{25}G^2$$

$$[1]_{\frac{1}{2}}=A-\tfrac{1}{2}\zeta_p+\tfrac{4}{25}F^2$$

As stated above the non-diagonal elements play a much more important rôle for nf than for ng. The influence of non-diagonal f_2' is usually dominating but the deviation from extreme pair coupling also implies larger G^{l-1} and G^{l+1} integrals, which are in some cases associated with rather large energy changes through non-diagonal g_{l-1}' and g_{l+1}'. Important non-diagonal matrix elements within each $(^3P)\,nf$ configuration are collected in Table 16. For $J=4\frac{1}{2}$ and $1\frac{1}{2}$ there are 3 levels involved in the $(^3P)\,nf$ secular equations and for $J=3\frac{1}{2}$ and $J=2\frac{1}{2}$ each 5 levels. The $J=3\frac{1}{2}$ equation is given below as an example.

$$\left|\begin{array}{ccc}
\nu-\nu_1^0 & +\frac{9\sqrt{3}}{56}G^2+\frac{145\sqrt{3}}{1512}G^4 & \frac{\sqrt{15}}{30}F^2-\frac{27\sqrt{15}}{280}G^2-\frac{17\sqrt{}}{151} \\
+\frac{9\sqrt{3}}{56}G^2+\frac{145\sqrt{3}}{1512}G^4 & \nu-\nu_2^0 & 0 \\
\frac{\sqrt{15}}{30}F^2-\frac{27\sqrt{15}}{280}G^2-\frac{17\sqrt{15}}{1512}G^4 & 0 & \nu-\nu_3^0 \\
0 & -\frac{\sqrt{15}}{50}F^2+\frac{3\sqrt{15}}{280}G^2+\frac{11\sqrt{15}}{504}G^4 & 0 \\
0 & \frac{2\sqrt{30}}{75}F^2-\frac{3\sqrt{30}}{140}G^2+\frac{\sqrt{30}}{378}G^4 & 0
\end{array}\right.$$

where 0 designates elements which are exactly zero or negligible and ν_1^0, ν_2^0, ν_3^0, ν_4^0, and ν_5^0 are energies calculated from the $(^3P_2)[4]_{3\frac{1}{2}}$, $(^3P_2)[3]_{3\frac{1}{2}}$, $(^3P_1)[4]_{3\frac{1}{2}}$, $(^3P_1)[3]_{3\frac{1}{2}}$, and $(^3P_0)[3]_{3\frac{1}{2}}$ diagonal expressions.

Occasionally the magnitudes of matrix elements and energy differences permit a simplification of the equations.

Results for* (^3P)*4f and 5f. The F^2, G^2, G^4, and B parameters calculated as described in the previous section are collected in Table 17, and the energies computed from them in Table 18. One column contains the energies from the diagonal expressions and the next those from the secular equations, the difference, consequently, representing the influence of non-diagonal elements. The contribution of non-diagonal $g'_{l\pm1}$ is in some cases considerable, firstly, when there are both non-diagonal f'_2 and $g'_{l\pm1}$ between two levels—which are in that case based on different parent levels—and, secondly, when there are non-diagonal $g'_{l\pm1}$ alone between two adjacent levels based on the same parent level. The most striking examples of the last kind are the $(^3P_2)[4]_{3\frac{1}{2}}$ $-(^3P_2)[3]_{3\frac{1}{2}}$ interactions for 4*f* and 5*f*. While the non-diagonal F^2 energies are 10 to 80 cm^{-1} for 4*f* the above non-diagonal $g'_{l\pm1}$ interaction corresponds to 8 cm^{-1}. For 5*f* the non-diagonal F^2 energies are between 3 and 20 cm^{-1}, while the above $(^3P_2)[4]_{3\frac{1}{2}}$–$(^3P_2)[3]_{3\frac{1}{2}}$ non-diagonal $g'_{l\pm1}$ interaction is 9 cm^{-1}.

It is seen from Table 18 that the theoretical and the observed energy level distributions are on the whole in good agreement. For 4*f* the differences are 0 to 16 cm^{-1}, and for 5*f* 1 to 11 cm^{-1}. It is evident that there is a substantial improvement in the over all agreement between the observed and the calculated energy values when the influence of the non-diagonal terms in the energy matrix is taken into account.

(^1D)*4f and* 5*f*. The theoretical distribution of the $(^1D)4f$ levels, as computed from the parameters derived from $(^3P)4f$, and the one observed are also consistent (Table 19). The agreement becomes still better with a somewhat smaller F^2 value. While the pairs should have zero splittings according to the theoretical diagonal expressions, neglecting the spin-orbit interaction of the outer electron, the observations show

Table 17. The F^2, G^2, G^4 and B parameters for $(^3P)4f$ and $5f$.

	F^2	G^2	G^4	B
4*f*	1 639.2	43.3	11.6	195 013.7
5*f*	835.1	35.8	9.3	205 041.7

$$\begin{array}{cc|l}
0 & 0 & \\
\frac{\sqrt{15}}{50}F^2+\frac{3\sqrt{15}}{280}G^2+\frac{11\sqrt{15}}{504}G^4 & \frac{2\sqrt{30}}{75}F^2-\frac{3\sqrt{30}}{140}G^2+\frac{\sqrt{30}}{378}G^4 & \\
0 & 0 & =0, \\
\nu-\nu_4^0 & 0 & \\
0 & \nu-\nu_5^0 &
\end{array}$$

splittings amounting to between 0.01 and 3 cm^{-1}. In the first place one should expect the splittings to be caused by non-diagonal elements between $({}^1D)4f$ and the adjacent $({}^3P)6f$ and $5f$ levels. Since there are no non-diagonal f_2' between $({}^1D)nf$ and $({}^3P)n'f$, the $g_{l\pm1}'$ elements alone have to be considered. A closer examination shows that there are no non-diagonal elements at all between $({}^1D)nf[5]_{5\frac{1}{2}}$, $[5]_{4\frac{1}{2}}$, or $[1]_{1\frac{1}{2}}$, $[1]_{\frac{1}{2}}$ and any other $n'f$ level;[1] consequently the levels of each of these pairs

Table 18. Comparison between observed and calculated $({}^3P)4f$ and $5f$ levels.

	$4f$			$5f$		
	ν (calc)*	ν (calc)	ν (obs)	ν (calc)*	ν (calc)	ν (obs)
$({}^3P_2)$ $[5]_{5\frac{1}{2}}$	195 123	123	124	205 097	097	101
$[5]_{4\frac{1}{2}}$	195 128	128	128	205 101	101	104
$[4]_{4\frac{1}{2}}$	194 850	814	800	204 959	949	938
$[4]_{3\frac{1}{2}}$	194 874	836	822	204 978	961	951
$[3]_{3\frac{1}{2}}$	194 902	867	883	204 987	985	996
$[3]_{2\frac{1}{2}}$	194 914	868	861	204 998	983	978
$[2]_{2\frac{1}{2}}$	195 093	022	031	205 086	071	079
$[2]_{1\frac{1}{2}}$	195 090	007	−004	205 084	061	056
$[1]_{1\frac{1}{2}}$	195 292	292	298	205 188	189	194
$[1]_{\frac{1}{2}}$	195 276	276	281	205 175	175	180
$({}^3P_1)$ $[4]_{4\frac{1}{2}}$	196 072	108	103	206 127	137	133
$[4]_{3\frac{1}{2}}$	087	117	119	139	146	149
$[3]_{3\frac{1}{2}}$	292	302	305	239	242	246
$[3]_{2\frac{1}{2}}$	302	313	316	248	252	255
$[2]_{2\frac{1}{2}}$	015	087	090	104	121	120
$[2]_{1\frac{1}{2}}$	000	082	076	091	113	103
$({}^3P_0)$ $[3]_{3\frac{1}{2}}$	196 590	622	622	206 617	625	624
$[3]_{2\frac{1}{2}}$	597	630	633	623	631	632

* Calculated from diagonal elements only.

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[1] From Tables 3 and 4 it is evident that the strong $({}^1D)3d\,{}^2G_{4\frac{1}{2}}$–$({}^1D)4f[5]_{5\frac{1}{2}}$ line in the vacuum ultraviolet has no $({}^1D)3d\,{}^2G_{4\frac{1}{2}}$–$({}^3P_2)4f[5]_{5\frac{1}{2}}$ counterpart (calculated wavenumber 40 942 cm^{-1}). This is in accordance with the fact that no non-diagonal energy matrix element exists between $({}^1D)nf[5]_{5\frac{1}{2}}$ and $({}^3P_2)nf[5]_{5\frac{1}{2}}$, which have equal J_c, l, K, and J values, and no non-diagonal element between $({}^1D)3d\,{}^2G_{4\frac{1}{2}}$ and any $({}^3P)nd$ level.

Table 19. Calculated and observed (^1D) $4f$ and $5f$ levels.

	$4f$		$5f$	
	ν (calc)	ν (obs)*	ν (calc)	ν (obs)*
($^1D_2$) [5]	208 809	803	218 943	941
[4]	209 353	338	219 220	
[3]	209 273	250	219 182	165?
[2]	208 913	922	219 002	003
[1]	208 530	592	218 810	

* Center of gravity.

should still coincide. The observations show that the [5] levels do so, whereas there is a small $[1]_{1\frac{1}{2}}$–$[1]_{\frac{1}{2}}$ splitting amounting to 0.3 cm^{-1}. The $[4]_{4\frac{1}{2},\,3\frac{1}{2}}$ pair, with an observed splitting of 0.3 cm^{-1}, should be influenced merely by g_4' elements, the $[2]_{2\frac{1}{2},\,1\frac{1}{2}}$ pair (splitting 2.2 cm^{-1}) by g_2' elements, while $[3]_{3\frac{1}{2},\,2\frac{1}{2}}$, with the largest splitting, 3 cm^{-1}, should be influenced by non-diagonal g_2' as well as g_4' elements.

In the (^1D)$5f$ group the $[5]_{5\frac{1}{2},4\frac{1}{2}}$ pair is observed with certainty; $[2]_{2\frac{1}{2},1\frac{1}{2}}$ might be correct, while $[3]_{3\frac{1}{2}}$ is uncertain. From Table 19 it is seen that there is a very good agreement between the observed [5] pair and that calculated from the (^3P)$5f$ parameters.

VI. Violations of the *K* selection rule for $4f$–ng transitions

The apparent break down of the K selection rule revealing itself through the comparatively strong ($^3P_2$)$4f[3]_{3\frac{1}{2}}$–($^3P_2$)$ng[5]_{4\frac{1}{2}}$ lines ($n = 5, 6, 7$) and the weaker ($^3P_2$)$4f[2]_{2\frac{1}{2}}$–($^3P_2$)$ng[4]_{3\frac{1}{2}}$ lines ($n = 5$ and 6) may be explained theoretically as follows. The non-diagonal $g_2'G^2 + g_4'G^4$ energy matrix element between the adjacent ($^3P_2$)$4f[3]_{3\frac{1}{2}}$ and ($^3P_2$)$4f[4]_{3\frac{1}{2}}$ levels indicates a mixing of the corresponding eigenfunctions. The resulting eigenfunctions may be written $\psi_i = a_i\psi_i^0 + a_k\psi_k^0$, where ψ_i^0 and ψ_k^0 are the "unperturbed" eigenfunctions. If the influence of other levels is negligible, then $a_i^2 + a_k^2 = 1$ as a consequence of the normalization conditions. The energy change corresponding to the mixing is obtained from $a_i(\nu_i - \nu_i^0) - a_k(g_2'G^2 + g_4'G^4) = 0$, where ν_i^0 is the energy according to the diagonal expression only. In the $4f$ case considered $\nu_i - \nu_i^0$ is approximately 8 cm^{-1} and $g_2'G^2 + g_4'G^4$ 14 cm^{-1}, giving $a_i \approx 0.9$ and $a_k \approx 0.5$. Consequently the eigenfunction associated with ($^3P_2$)$4f[3]_{3\frac{1}{2}}$ is approximately a combination of the form

$$\psi(4f[3]_{3\frac{1}{2}}) = 0.9\,\psi^0(4f[3]_{3\frac{1}{2}}) + 0.5\,\psi^0(4f[4]_{3\frac{1}{2}}).$$

The strength of the ($^3P_2$)$4f[3]_{3\frac{1}{2}}$–($^3P_2$)$ng[5]_{4\frac{1}{2}}$ transition depends on the matrix element of the dipole moment, $\int \psi(4f[3]_{3\frac{1}{2}})P\psi(ng[5]_{4\frac{1}{2}})\,d\tau$, which can be written

$$0.9 \int \psi^0(4f[3]_{3\frac{1}{2}})P\psi(ng[5]_{4\frac{1}{2}})\,d\tau + 0.5 \int \psi^0(4f[4]_{3\frac{1}{2}})P\psi(ng[5]_{4\frac{1}{2}})\,d\tau.$$

In this expression only the first integral is zero and therefore the $({}^3P_2)4f[3]_{3\frac{1}{2}}$–$({}^3P_2)ng[5]_{4\frac{1}{2}}$ lines exist.

The $({}^3P_2)ng[5]_{4\frac{1}{2}}$ and $[4]_{4\frac{1}{2}}$ levels are certainly very close to each other, and there are non-diagonal $g_3'G^3 + g_5'G^5$ elements between them, but the $(\nu_i - \nu_i^0)/(g_3'G^3 + g_5'G^5)$ ratio is small and therefore the mixing of eigenfunctions is much smaller than in the $4f$ case treated above.

The appearance of the $4f[3]_{3\frac{1}{2}}$–$ng[5]_{4\frac{1}{2}}$ lines implies a decreased $4f[4]_{3\frac{1}{2}}$–$ng[5]_{4\frac{1}{2}}$ intensity (Tables 6, 7, and 8) and, analogously, part of the $4f[3]_{3\frac{1}{2}}$–$ng[4]_{4\frac{1}{2}}$ intensity is transferred to $4f[4]_{3\frac{1}{2}}$–$ng[4]_{4\frac{1}{2}}$, the first transitions being unexpectedly weak and the second ones abnormally strong. A similar reciprocity is observed for $4f[3]_{3\frac{1}{2}}$–$ng[3]_{3\frac{1}{2}}$ and $4f[4]_{3\frac{1}{2}}$–$ng[3]_{3\frac{1}{2}}$.

The observed weak $4f$–ng transitions between levels based on different ${}^3P_{2,1,0}$ parent levels are associated with the occurrence of non-diagonal $f_2'F^2$ elements, the largest mixing being between $({}^3P_2)4f[2]$ and $({}^3P_1)4f[2]$.

VII. Determination of the ionization limits

The determination of a reliable ionization limit requires at least one series of energy levels with no, or at least small, perturbations. Occasionally it is possible to find a series of energy sums for which the influence of perturbations is eliminated. A thorough examination of possible perturbations is particularly important for electronic systems like that of Ar II, where the observations show large irregularities as a consequence of configuration interaction. Generally, the magnitude of the perturbations is $(-f_2'F^2 + g_{l-1}'G^{l-1} + g_{l+1}'G^{l+1})^2/(\nu_i - \nu_k)$, where the F^2, G^{l-1}, and G^{l+1} integrals are common to all interactions between the levels of two given configurations. From the present investigation and from as yet unpublished results for lower l values it is evident that the F and G integrals associated with a separate configuration decrease as l of the external electron increases. The same should hold for the analogous integrals between configurations with equal l but different n values and, therefore, for a given ν_i–ν_k interval, the perturbations should also decrease. This is to some extent experimentally verified by comparing the pair splittings of the $({}^1D)nf$ and $({}^1D)ng$ levels; while the levels of the $({}^1D)ng$ pairs almost coincide, there is a splitting of a $({}^1D)nf$ pair amounting to 3 cm^{-1}. The ng and then the nf series should, consequently, be favourable in computing the ionization limits but for the risk of electric dipole interactions (Stark effect). This, in turn, is connected with the properties of the light source; in the present case, employing a low-pressure high-frequency discharge, the observed $4f$–ng lines ($n = 5$, 6, and 7) are sharp, showing no signs of Stark effect influence.

The discussion of interactions between configurations with equal l and with arbitrary n quantum numbers may be based on the non-diagonal f_2', g_{l-1}', and g_{l+1}' coefficients, since, in deriving them, no assumption is made concerning the n quantum number, which, in return, is accounted for in the F^2, G^{l-1} and G^{l+1} integrals. Consequently, the f_2', g_{l-1}', and g_{l+1}' coefficients are independent of n; they are based solely on the angular parts of the eigenfunctions. The conclusion, therefore, is that *if there are no non-diagonal matrix elements between a certain level and any other level of the same configuration, then there is no interaction between the level considered and analogous configurations with different n values.* A series of such levels is consequently unaffected by interactions from analogous configurations. From the tables of non-diagonal f_2',

g'_{l-1}, and g'_{l+1} coefficients it is realized that the following ng series fulfil this requirement: $(^3P_2)[6]_{6\frac{1}{2}}$, $(^3P_2)[2]_{1\frac{1}{2}}$, $(^1D_2)[6]_{6\frac{1}{2},5\frac{1}{2}}$ and $(^1D_2)[2]_{2\frac{1}{2},1\frac{1}{2}}$. The $(^3P_2)ng[6]_{6\frac{1}{2}}$ series, for example, should not be influenced by $(^3P)ng$ or by $(^1D)ng$ or $(^1S)ng$ levels or corresponding continua. There are no non-diagonal f'_2 between levels based on ^3P and those based on ^1D or ^1S, and no non-diagonal g'_3 or g'_5 between levels with $J = l + 2\frac{1}{2}$ or between levels with $J = l - 2\frac{1}{2}$. The influence on $(^3P_2)[6]_{5\frac{1}{2}}$ should be very small, since it is affected only by a non-diagonal G^5 element.

Concerning the interactions between ng and configurations with the same parity but with a different l value it is obvious that nd cannot affect $ng[6]_{6\frac{1}{2},5\frac{1}{2}}$ since no nd level has a J as high as $5\frac{1}{2}$ and that an appreciable ng–ni interaction is improbable even for $n = 7$. Since at most two members of the $(^1D)ng$ series have been observed, the most reliable ng series for an ionization limit determination should be $(^3P_2)ng[6]_{6\frac{1}{2}}$ and, thereafter, $(^3P_2)ng[2]_{1\frac{1}{2}}$ and $(^3P_2)ng[6]_{5\frac{1}{2}}$ from a theoretical point of view. As regards the observations it should be pointed out that the $(^3P_2)4f[5]_{5\frac{1}{2}}$–$(^3P_2)ng[6]_{6\frac{1}{2}}$ wavelengths might be slightly influenced by the unresolved $4f[5]_{5\frac{1}{2}}$–$ng[6]_{5\frac{1}{2}}$ satellites.

An analogous discussion of the nf series indicates $(^3P_2)nf[5]_{5\frac{1}{2}}$ and, then, $(^3P_2)[1]_{\frac{1}{2}}$ and $(^3P_2)[5]_{4\frac{1}{2}}$ as suitable. In the case of Ar II, however, the $[1]_{\frac{1}{2}}$ series could not be used since only two members were observed, and $[5]_{5\frac{1}{2}}$ had to be abandoned since the third level ($n = 6$) was calculated from a single line in the vacuum ultraviolet, implying comparatively low wavenumber accuracy.

It should be possible to reduce the influence of configuration interaction on other series by forming the sums of interacting levels. In the nf and ng series of Ar II the large interactions occur between levels with equal n values based on the $^3P_{2,1,0}$ parents and, therefore, the sums should for each n contain (^3P) levels with equal J values, i.e. the same sums that were used in calculating the F^2, G^{l-1}, and G^{l+1} parameters in Section V.

Results. The previous examination shows that the $(^3P_2)ng[6]_{6\frac{1}{2}}, [6]_{5\frac{1}{2}}, [2]_{1\frac{1}{2}}$ and $(^3P_2)nf[5]_{4\frac{1}{2}}$ series should be unperturbed or very slightly perturbed and, at the same time, well-established and accurately connected to the ground term $3p^5\,^2P$. The following sums of levels have similar properties: $\Sigma(^3P)ng$, $J = 5\frac{1}{2}$ and $J = 3\frac{1}{2}$, $\Sigma(^3P)nf$, $J = 2\frac{1}{2}$. The limits were derived by means of Ritz formulas; the level sums gave the corresponding sums of limits, from which the separate limits can be obtained from the $3p^4\,^3P_{2,1,0}$ intervals observed in Ar III. For comparison the limits were also computed from other accurate nf and ng series. The $^3P_2$ limit given by the $ng[6]_{6\frac{1}{2}}$ series is 222 848.16 cm^{-1} above the ground level $3p^5\,^2P_{1\frac{1}{2}}$; $ng[6]_{5\frac{1}{2}}$ and $[2]_{1\frac{1}{2}}$ give values which are 0.4 cm^{-1} higher. Remaining $(^3P_2)ng$ series give limits which differ from the above value by -0.2 to $+1.2$ cm^{-1}, whereas the $J = 5\frac{1}{2}$ sums give a limit which agrees almost exactly with the 222 848.16 value; the $J = 3\frac{1}{2}$ sum series gives a value which is lower by about 0.4 cm^{-1}. The $(^3P_2)nf[5]_{4\frac{1}{2}}$ series limit was found to be 0.9 cm^{-1} lower; some other nf series also give lower values, the largest difference being 2.5 cm^{-1}, while the Σnf, $J = 2\frac{1}{2}$ series corresponds to a value which is lower by 1.9 cm^{-1}. Thus the $^3P_2$ limit obtained from good ng series is between 222 847.8 and 222 848.6 cm^{-1}, while the most reliable nf series gives 222 847.2. Since the ng series should be less sensitive to perturbations, the value obtained from the $ng[6]_{6\frac{1}{2}}$ series was adopted as the most accurate one, rounded off to 222 848.2. The remaining series limits were computed from the $3p^4$ intervals observed in Ar III:

$^3P_2$: 222848.2	$^1D_2$: 236858.2
$^3P_1$: 223960.3	
$^3P_0$: 224418.4	$^1S_0$: 256113.9

The Ar II series and their limits will be further discussed in a forthcoming paper.

SUMMARY

The continued analysis of the spectrum of singly ionized argon based on new observations in the whole 12500–500 Å range has given about 180 new energy levels. Some 120 of them belong to the $3p^4nf$ and ng configurations.

The spectrum was excited by means of high-frequency pulses in a discharge tube containing argon gas at low pressure.

The present part of the investigation is concerned with the nf and ng configurations. A pronounced pair coupling was observed for ng and an approximate pair coupling for nf. The combinations of nf with other configurations and those of ng with $4f$ have been studied from an observational point of view as regards selection rules and estimated intensities.

The p^4l system belongs to the "two holes in a closed shell and one outer electron" configurations recently investigated theoretically by N. H. Möller [2]. The comparison of observed level positions with the theoretical distribution shows good agreement for ng. In the case of nf the discrepancies are larger, which probably has to do with the much larger rôle played by non-diagonal energy matrix elements between levels with different values of n.

On the basis of the theoretical results as regards the influence of non-diagonal matrix elements and the corresponding mixing of eigenfunctions an explanation is given for the apparent breakdown of the K selection rule for certain $(^3P)4f$–$(^3P)ng$ transitions.

On the same basis the reliability of nf and ng series for an accurate determination of the ionization limit is discussed. The subsequent calculation of the $^3P_2$ limit from $(^3P_2)ng[6]_{6\frac{1}{2}}$ involves an adjustment of the previously adopted value by about 28 cm^{-1}, which means that the $3p^4\,^3P_2$ ionization limit is 222848.2 cm^{-1} above the $3p^5\,^2P_{1\frac{1}{2}}$ ground level.

An examination of the non-diagonal matrix elements between levels based on different parent levels shows that some series based on $^1D_2$ should exist above the $^3P_2$ limit. One pair of coincident levels, $(^1D_2)6g[6]_{6\frac{1}{2},5\frac{1}{2}}$, has possibly been found.

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Note added in proof.—The $g'_{l\pm1}$ coefficients in the present paper are based on the $\bar{g}'_{l\pm1}$ expressions originally communicated by N. H. Möller to the author. It was later discovered that the $\bar{g}'_{l\pm1}$ coefficients given then should be multiplied by a factor of $\frac{1}{2}$; this was corrected in proof in Möller's tables, but it was too late to change all $g'_{l\pm1}$ expressions in the present paper. The factor $\frac{1}{2}$ does not, however, affect the calculation of the energy level distribution, since the $g'_{l\pm1}\,G^{l\pm1}$ products remain unchanged. The only effect is that the $G^{l\pm1}$ parameters given in Tables 11 and 17 are half as large as those defined in TAS.

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